

ORIGINAL

Application Based on

Docket **87742AEK**

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ORGANIC ELEMENT FOR ELECTROLUMINESCENT DEVICES

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Express Mail Label No.: EV293530202US

Date: March 16, 2004

ORGANIC ELEMENT FOR ELECTROLUMINESCENT DEVICES

FIELD OF THE INVENTION

This invention relates to an electroluminescent (EL) device comprising a light-emitting layer containing a rubrene derivative containing
5 fluorine or fluorine-containing groups.

BACKGROUND OF THE INVENTION

While organic electroluminescent (EL) devices have been known for over two decades, their performance limitations have represented a barrier to many desirable applications. In simplest form, an organic EL device is comprised
10 of an anode for hole injection, a cathode for electron injection, and an organic medium sandwiched between these electrodes to support charge recombination that yields emission of light. These devices are also commonly referred to as organic light-emitting diodes, or OLEDs. Representative of earlier organic EL devices are Gurnee et al. US 3,172,862, issued Mar. 9, 1965; Gurnee US
15 3,173,050, issued Mar. 9, 1965; Dresner, "Double Injection Electroluminescence in Anthracene", *RCA Review*, **30**, 322-334, (1969); and Dresner US 3,710,167, issued Jan. 9, 1973. The organic layers in these devices, usually composed of a polycyclic aromatic hydrocarbon, were very thick (much greater than 1 μm). Consequently, operating voltages were very high, often greater than 100V.

20 More recent organic EL devices include an organic EL element consisting of extremely thin layers (e.g., less than 1.0 μm) between the anode and the cathode. Herein, the term "organic EL element" encompasses the layers between the anode and cathode. Reducing the thickness lowered the resistance of the organic layer and has enabled devices that operate at much lower voltage. In a
25 basic two-layer EL device structure, described first in US 4,356,429, one organic layer of the EL element adjacent to the anode is specifically chosen to transport holes, and therefore, it is referred to as the hole-transporting layer, and the other organic layer is specifically chosen to transport electrons, and is referred to as the electron-transporting layer. Recombination of the injected holes and electrons
30 within the organic EL element results in efficient electroluminescence.

There have also been proposed three-layer organic EL devices that contain an organic light-emitting layer (LEL) between the hole-transporting layer and electron-transporting layer, such as that disclosed by Tang et al (*J. Applied Physics*, **65**, Pages 3610-3616, (1989)). The light-emitting layer commonly consists of a host material doped with a guest material, also known as a dopant. Still further, there has been proposed in US 4,769,292 a four-layer EL element comprising a hole-injecting layer (HIL), a hole-transporting layer (HTL), a light-emitting layer (LEL) and an electron transport/injection layer (ETL). These structures have resulted in improved device efficiency.

Since these early inventions, further improvements in device materials have resulted in improved performance in attributes such as color, stability, luminance efficiency and manufacturability, e.g., as disclosed in US 5,061,569, US 5,409,783, US 5,554,450, US 5,593,788, US 5,683,823, US 5,908,581, US 5,928,802, US 6,020,078, and US 6,208,077, amongst others.

Notwithstanding these developments, there are continuing needs for organic EL device components, such as light-emitting materials, sometimes referred to as dopants, that will provide high luminance efficiencies combined with high color purity and long lifetimes. In particular, there is a need to be able to adjust the emission wavelength of the light-emitting material for various applications. For example, in addition to the need for blue, green, and red light-emitting materials there is a need for blue-green, yellow and orange light-emitting materials in order to formulate white-light emitting electroluminescent devices. For example, a device can emit white light by emitting a combination of colors, such as blue-green light and red light or a combination of blue light and orange light.

White EL devices can be used with color filters in full-color display devices. They can also be used with color filters in other multicolor or functional-color display devices. White EL devices for use in such display devices are easy to manufacture, and they produce reliable white light in each pixel of the displays. Although the OLEDs are referred to as white they can appear white or off-white, the CIE coordinates of the light emitted by the OLED are less important than the

requirement that the spectral components passed by each of the color filters be present with sufficient intensity in that light. The devices must also have good stability in long-term operation. That is, as the devices are operated for extended periods of time, the luminance of the devices should decrease as little as possible.

5 A useful class of dopants is that derived from 5,6,11,12-tetraphenylnaphthacene, also referred to as rubrene. The solution spectra of these materials are typically characterized by wavelength of maximum emission, also referred to as emission λ_{max} , in a range of 550-560 nm and are useful in organic EL devices in combination with dopants in other layers to produce white light.

10 Use of these rubrene-derived dopants in EL devices depends on whether the material sublimates. If the material melts, its use as a dopant is limited. Sublimation and deposition are the processes by which the dopant, subjected to high temperature and low pressure passes from the solid phase to the gas phase and back to the solid phase and in the process is deposited onto the device.

15 Depending on the chemical structure of the dopant, when the temperature needed to sublime the dopant is high, thermal decomposition can occur. If the decomposition products also sublime the device can become contaminated. Decomposition leads to the inefficient use of dopant. Contamination with decomposition products can cause the device to have shorter operational lifetimes

20 and can contribute to color degradation and light purity. In order to achieve OLEDs that can produce high purity white light, have good stability and no contamination from dopant decomposition, in addition to efficient use of dopant, one needs to have the ability to lower the sublimation temperature.

 Useful dopants are those that emit light in ethyl acetate solution in

25 the range of 530-650nm, have good efficiency and sublime readily.

 US 6,387,547B1; US 6,399,223B1; and EP 1,148,109A2 teaches the use of rubrene derivatives containing either 2 phenyl groups on one end ring of the rubrene structure or 4 phenyl groups on both end rings. There is no teaching of fluorine or fluorine-containing groups on the rubrene structure.

30 JP 04335087A discloses specific compounds 6, 13 and 14 containing chlorine or bromine at various positions on the rubrene molecule.

WO 02100977A1 discloses compound "C12" with two heterocyclic aromatic fluorine-containing groups also on the 5- and 12-positions of the naphthacene nucleus.

JP 10289786A discloses compound "15" with fluoro- groups on the
5 para-positions of the secondary phenyl rings at the 5- and 12-positions of the naphthacene nucleus. US Ser No. 10/700,894 filed November 4, 2003, describes fluorine containing rubrenes for lowering the sublimation temperature where there are certain fluoro group arrangements.

However, high sublimation temperatures and possible
10 decomposition would limit the use of many of these rubrene derivatives. Some of these materials would also be limited in the range of hues that they could provide. Devices containing many rubrene derivatives would fail to provide consistent white OLED devices with high color purity and reduced potential for possible contamination from decomposition impurities in their deposition. It is a problem
15 to be solved to provide an OLED device using materials that can be sublimed at a lower temperature thus providing a lowered level of decomposition during the vacuum deposition process.

SUMMARY OF THE INVENTION

20 The invention provides an electroluminescent device comprising a host material and a rubrene derivative having a naphthacene nucleus comprising four fused phenyl rings a, b, c, and d, in order, containing two secondary phenyl ring groups linked to the "c" ring, each bearing directly or indirectly a fluoro or perfluoroalkyl group, wherein each fluoro or perfluoroalkyl group is either:

25 a) linked directly to one of said secondary phenyl rings and is located on a meta or ortho position, or

b) located in any position of another aryl group linked directly or indirectly to one of the secondary phenyl rings.

The invention also provides displays and area lighting devices
30 containing the device and a process for emitting light employing the device. The device is advantageous because the materials can be sublimed at a lower

temperature thus providing a lowered level of decomposition during a vacuum deposition process.

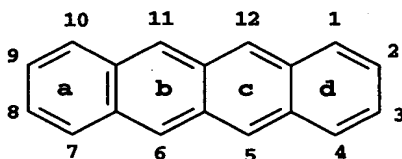
BRIEF DESCRIPTION OF THE DRAWINGS

5 FIG. 1 shows a cross-section of a typical OLED device in which this invention may be used.

DETAILED DESCRIPTION OF THE INVENTION

 An electroluminescent device of the invention may be a multilayer device comprising a cathode, an anode, charge-injecting layers (if necessary),
10 charge-transporting layers, and a light-emitting layer (LEL) comprising a host and at least one light-emitting material. Desirably the light-emitting layer comprises a host material and a rubrene derivative.

 The term rubrene refers to a 5,6,11,12-tetraphenylnaphthacene as defined by the *Grant & Hackh's Chemical Dictionary*, Fifth Edition, McGraw-Hill
15 Book Company, page 512 and *Dictionary of Organic Compounds*, Fifth Edition, Chapman and Hall, Volume 5, page 5297. The term naphthacene is the chemical name used to describe four linearly fused benzene rings as defined by the *Grant & Hackh's Chemical Dictionary*, Fifth Edition, McGraw-Hill Book Company, page 383. The four rings of the rubrene naphthacene nucleus can be labeled as the a, b,
20 c, and d rings as shown below.



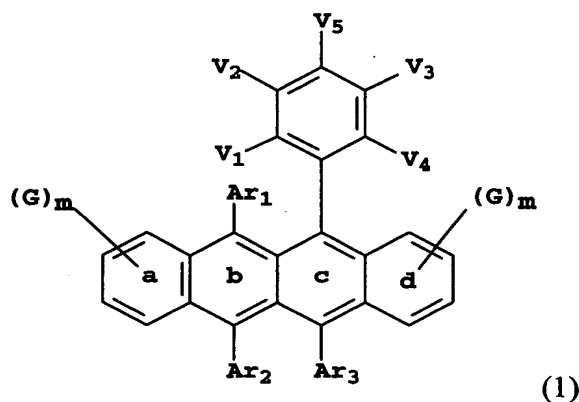
 In one desirable embodiment the rubrene derivative of the
25 invention contains at least one phenyl ring on the "c" ring bearing a fluoro group or a fluorine containing alkyl group on a meta or ortho position of that phenyl ring. In one embodiment, the fluorine containing alkyl group is a perfluoroalkyl group,

which is an alkyl group that is fully substituted with fluoro substituents, for example a trifluoromethyl or pentafluoroethyl group.

In another desirable embodiment the rubrene derivative of the invention contains at least one secondary phenyl ring on the "c" ring, which is
5 linked to, that is substituted with, a further aryl group. Alternatively, the phenyl ring may be indirectly linked to the aryl ring. That is the secondary phenyl ring may be bonded to another group, which in turn may be bonded to the aryl ring. The aryl group contains a fluoro or perfluoroalkyl substituent. In this case the fluoro or perfluoroalkyl group is not restricted to be in a meta or ortho position of
10 the aryl group. The term aryl group is intended to include only aromatic groups of one or more than one fused rings having only carbon ring members and not heteroatomic group ring members.

In one desirable embodiment, the aryl group is a phenyl group that is substituted with a fluoro or perfluoroalkyl group, suitably the phenyl group is
15 substituted with a meta- or para-fluoro substituent.

Desirably, the rubrene derivative is represented by Formula (1).



In Formula (1) Ar₁, Ar₂, and Ar₃ represent independently selected
20 aryl groups, for example phenyl groups or tolyl groups. Each G represents an independently selected substituent, such as an alkyl group, for example a methyl group. Each m is independently 0-4. In Formula (1), V¹ – V⁵ represent hydrogen

or independently selected substituent groups, such as an alkyl or an aryl groups, provided there are in total two fluoro or perfluoroalkyl groups linked directly or indirectly to the "c" ring, selected from those where at least one of $V^1 - V^4$ represents a fluoro or perfluoroalkyl group, or at least one of $V^1 - V^5$ and AR_3 includes an aryl group bearing a fluoro or trifluoromethyl group.

In one suitable embodiment, V^3 of Formula 1 represents a fluoro substituent. In another suitable embodiment, at least one of V^2 , V^3 , and V^5 includes a phenyl ring bearing a fluoro or perfluoroalkyl group.

Substituents on the rubrene derivative of the invention are selected to provide embodiments that exhibit a reduced loss of initial luminance compared to the device containing no naphthacene compound.

Embodiments of the dopants useful in the invention provide an EL device emitting light with yellow, yellow-orange, orange, orange-red or red hues. Suitably the substituents of the rubrene derivative are selected to provide an emitted light having a wavelength of maximum emission (λ_{max}) in ethyl acetate solution such that λ_{max} is greater or equal to 520 nm and less than or equal to 650 nm, have good efficiency and sublime at low temperatures. Combined with other light-emitting dopants, the dopants of the invention can be used to produce white light.

In one embodiment, the substituents of the rubrene derivative are selected to provide an emitted light having an orange-red hue. The rubrene derivative may be used in a device that also comprises another light-emitting dopant that emits blue or blue-green light.

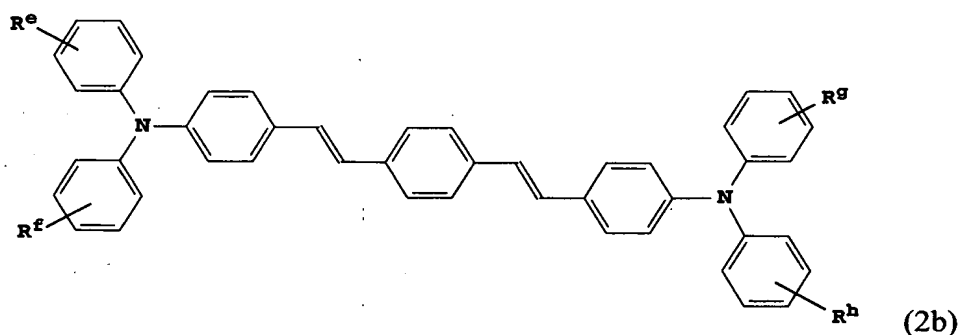
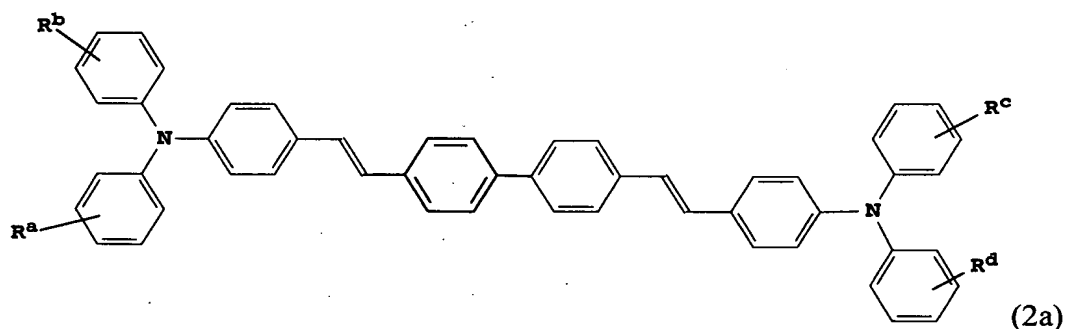
Blue light is generally defined as having a wavelength range in the visible region of the electromagnetic spectrum of 450-480 nm, blue-green 480-510 nm, green 510-550, green-yellow 550-570 nm, yellow 570-590 nm, orange 590-630 nm and red 630-700 nm, as defined by Dr. R.W.G.Hunt in *The Reproduction of Colour in Photography, Printing & Television*, 4th Edition 1987, Fountain Press, page 4. Suitable combinations of these components produce white light. When light has a spectral profile that overlaps these ranges, to whatever degree, it

is loosely referred to as having both color components for example, yellow-orange or orange-red.

Many materials that emit blue or blue-green light are known in the art and are contemplated for use in the practice of the present invention.

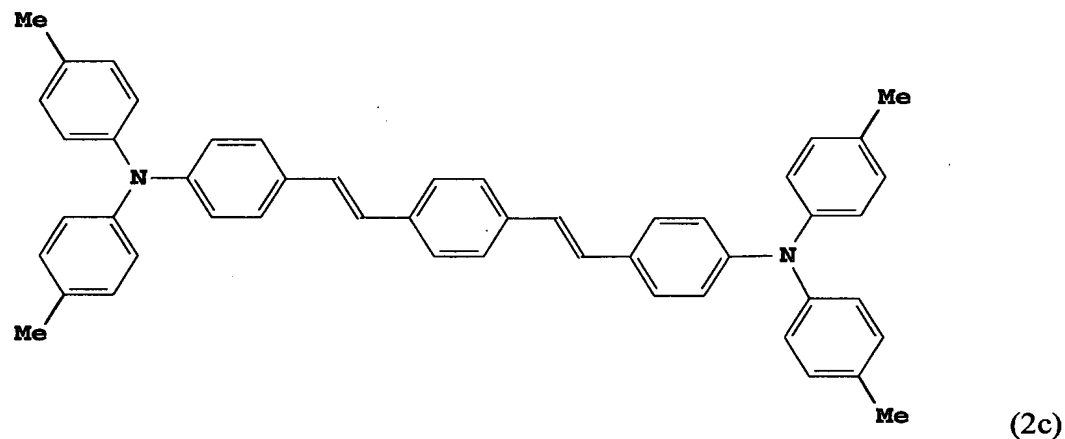
- 5 Particularly useful classes of blue emitters include perylene and its derivatives such as a perylene nucleus bearing one or more substituents such as an alkyl group or an aryl group. A desirable perylene derivative for use as a blue emitting material is 2,5,8,11-tetra-*t*-butylperylene.

- Another useful class of fluorescent materials includes blue or blue-green light emitting derivatives of distyrylarenes, such as distyrylbenzene and distyrylbiphenyl, including compounds described in US 5,121,029. Among derivatives of distyrylarenes that provide blue or blue-green luminescence, particularly useful are those substituted with diarylamino groups, also known as distyrylamines. Examples include Formula 2a and 2b, listed below, wherein R^a –
15 R^j can be the same or different, and individually represent hydrogen or one or more substituents. For example, substituents can be alkyl groups, such as methyl groups, or aryl groups, such as phenyl groups.

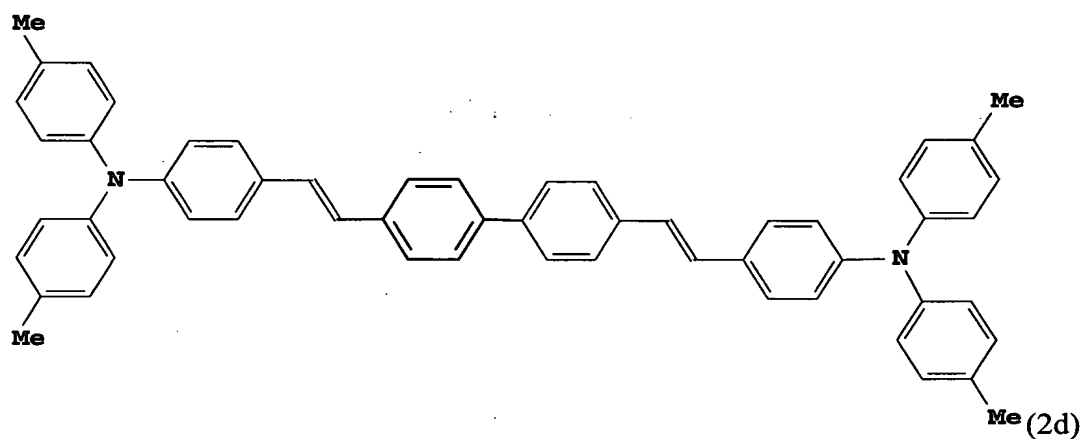


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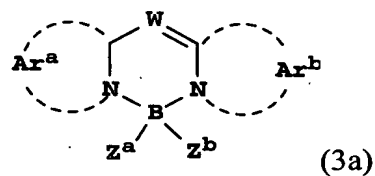
Illustrative examples of useful distyrylamines are blue or blue green emitters, (2c) and (2d) listed below.



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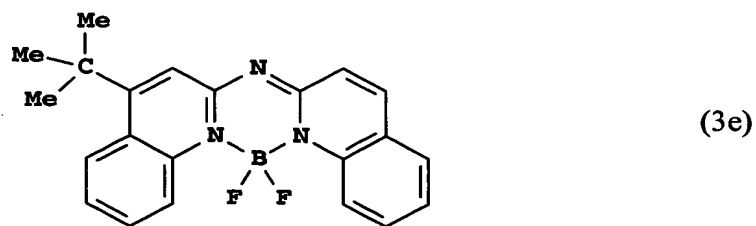
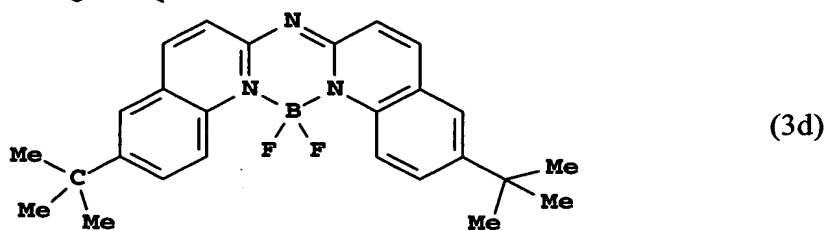
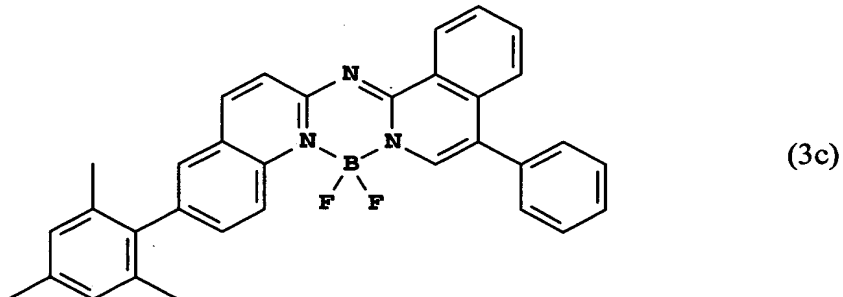
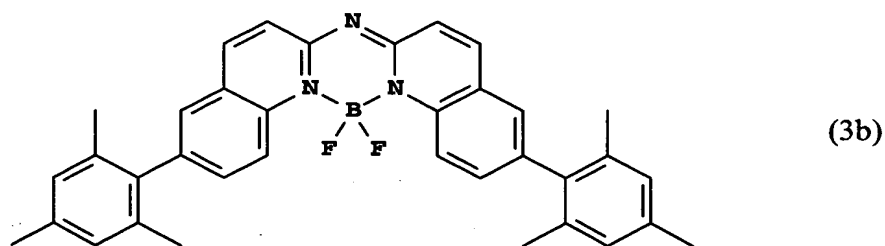
Another useful class of blue or blue green emitters comprise a boron atom. Desirable light-emitting materials that contain boron include those described in US 20030198829A1 and US 20030201415A1. Suitable blue or blue-green light-emitting materials are represented by the structure Formula (3a).

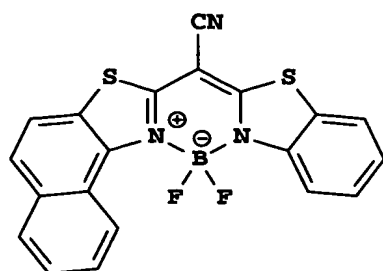


In Formula (3a), Ar^a and Ar^b independently represent the atoms necessary to form a five or six-membered aromatic ring group, such as a pyridine group. Z^a and Z^b represent independently selected substituents, such as fluoro substituents. In Formula (3a), w represents N or C-Y, wherein Y represents hydrogen or a substituent, such as an aromatic group, such as a phenyl group or a tolyl group, an alkyl group, such as a methyl group, a cyano substituent, or a trifluoromethyl substituent.

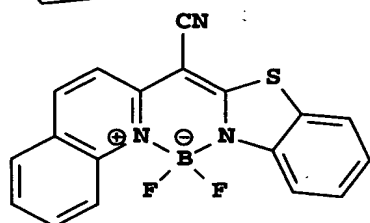
Illustrative examples of useful boron-containing blue fluorescent materials are listed below.

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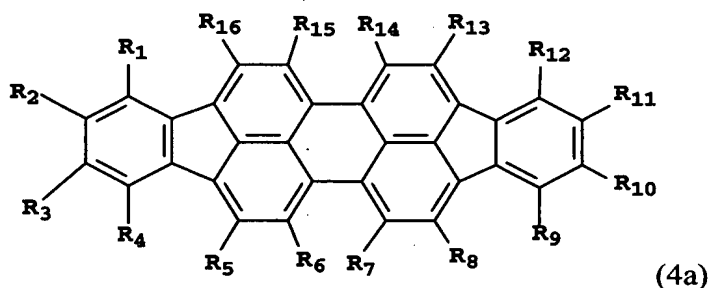
3f



3g

In one embodiment of the invention, the device further comprises a red-light-emitting compound to provide a white light emission. In one desirable embodiment the red-light-emitting compound is a diindenoperylene compound of

5 Formula (4a).



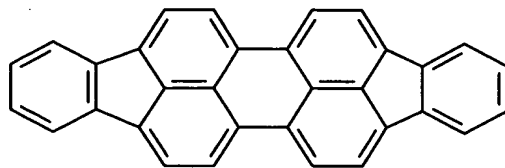
In Formula (4a), R₁-R₁₆ are independently selected as hydrogen or substituent groups that provide red luminescence; see, for example, U.S. Patent

10 Application Serial No 10/334,324, and provided that any of the indicated substituents can join to form further fused rings.

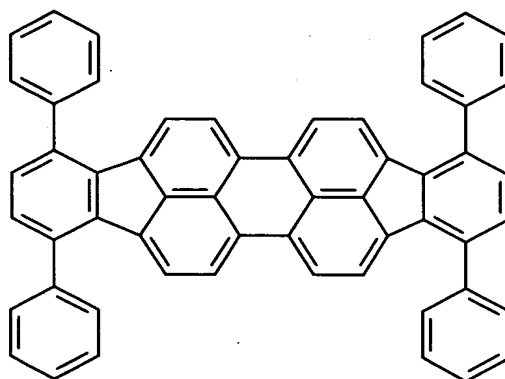
Particularly useful diindenoperylene dopants that provide red luminescence are those in which R₁ – R₁₆ are independently selected from the category including hydrogen and aryl groups, including aryl ring groups fused to

15 the diindenoperylene skeleton, as illustrated by the formulas shown below. In one desirable embodiment R₁, R₄, R₉, R₁₂ of Formula (4a) represent independently

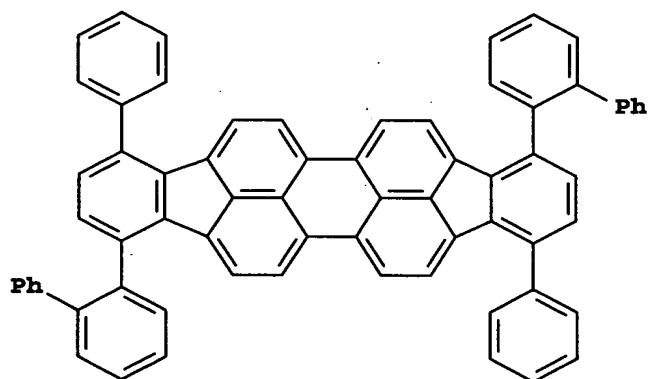
selected phenyl groups, R_2 , and R_3 as well as R_{10} and R_{11} form independently selected fused benzene ring groups.



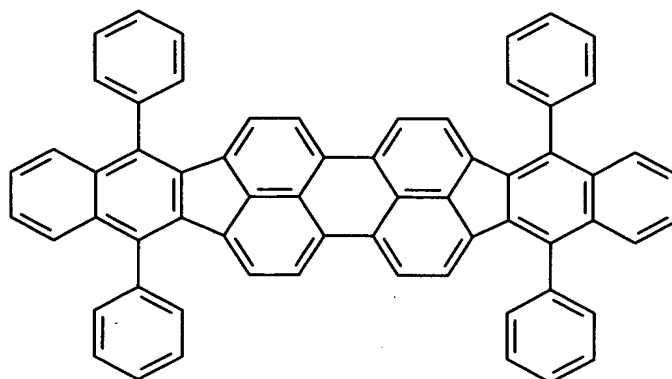
4b



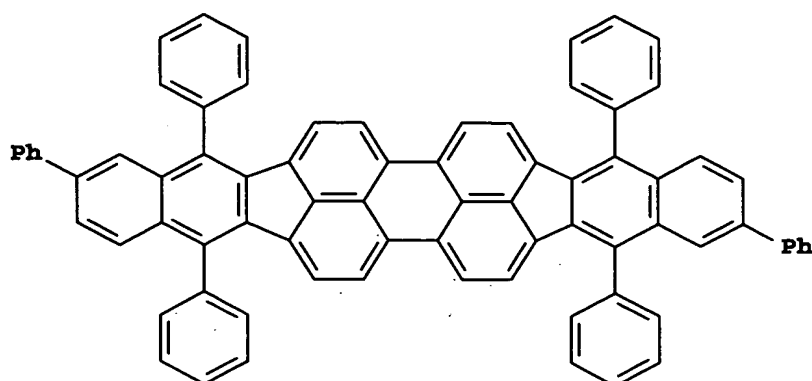
4c



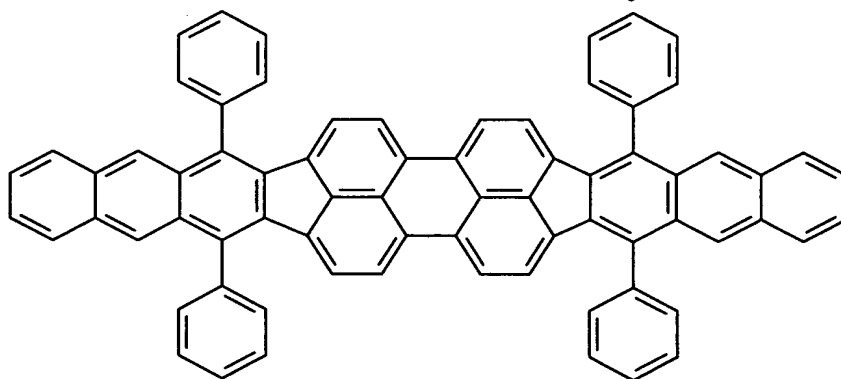
4d



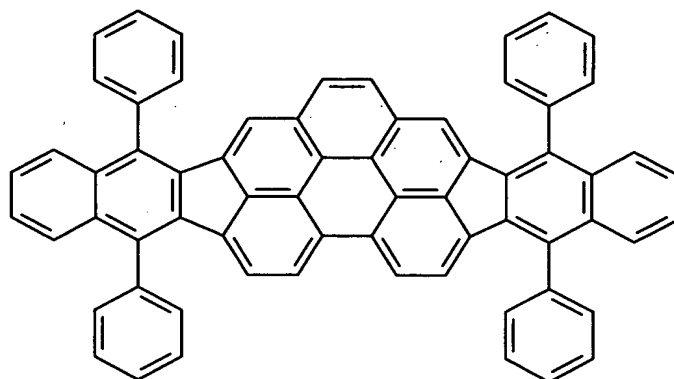
4e



4f



4g



4h

When a material of Formula (4a) is present, the rubrene derivative of the invention may not emit light, but instead transfer energy to the diindenoperylene derivative of Formula (4a), which in turn emits red light.

The electroluminescent device comprises, in addition to a rubrene derivative, a host material. Suitably, the rubrene derivative is present in an amount of up to 25%-wt of the host, typically up to 15% and more typically up to 10% and commonly from 0.1-5.0%-wt of the host.

The host may be a hole-transporting material. For example the host may be a tertiary amine or a mixture of such compounds. Examples of useful hole-transporting materials are 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB), and 4,4'-bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]biphenyl (TNB).

5 The host may be an electron-transporting material. Metal complexes of 8-hydroxyquinoline and similar derivatives, also known as metal-chelated oxinoid compounds, constitute a class of useful host compounds. An especially useful example of electron-transporting host material is tris(8-quinolinolato)aluminum(III) (AlQ).

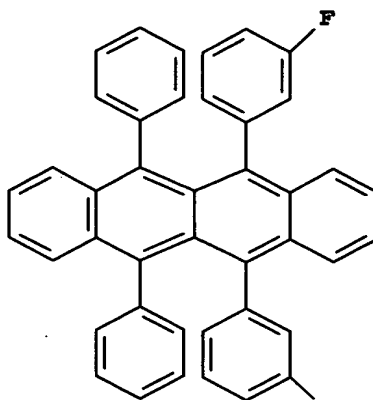
10 In another embodiment of the invention, when additional layers are present so that the emitted light is white, a filter capable of controlling the spectral components of the white light such as red, green and blue, can be placed overlying the device to give a device useful for color display.

 The rubrene derivative may also be an oligomer or a polymer
15 having a main chain or a side chain of repeating units. The rubrene derivative may be provided as a discrete material dispersed in the host material, or it may be bonded in some way to the host material, for example, covalently bonded into a polymeric host. In one useful embodiment, at least one layer of the EL device, comprises polymeric material. In another suitable embodiment, at least two layers
20 of the EL device comprise polymeric material.

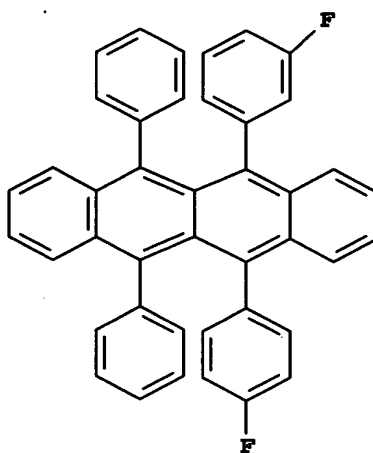
 Rubrene derivatives useful in the present invention may be synthesized by various methods known in the literature. For example see J. Dodge, J. Bain, R. Chamberlin, *J. of Org. Chem.*, **55**, 4190 (1990) and A. Essenfeld, US 4,855,520 and references cited therein.

25 Illustrative examples of rubrene derivatives useful in the present invention include the following compounds.

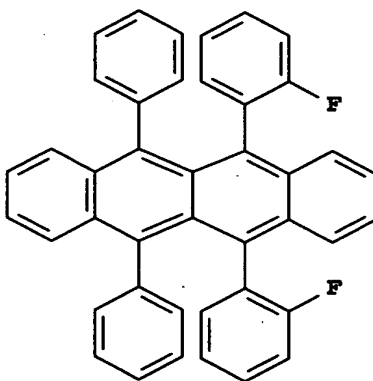
Inv-1



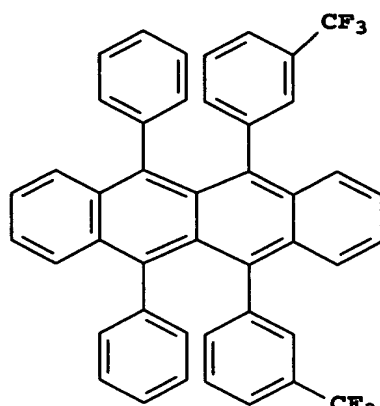
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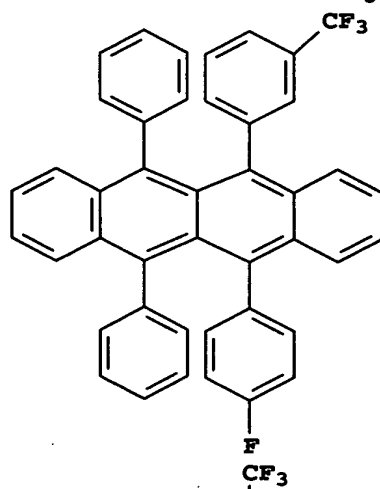
Inv-3



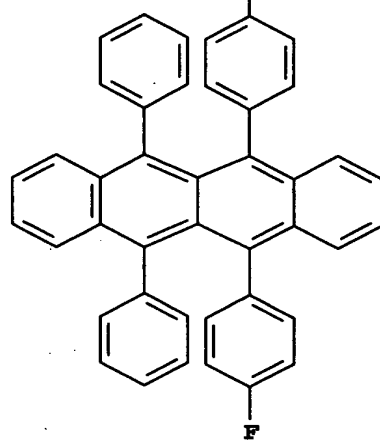
Inv-4



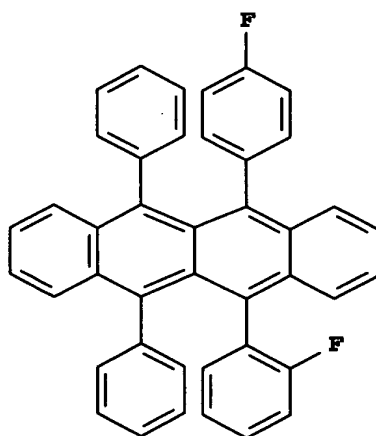
Inv-5



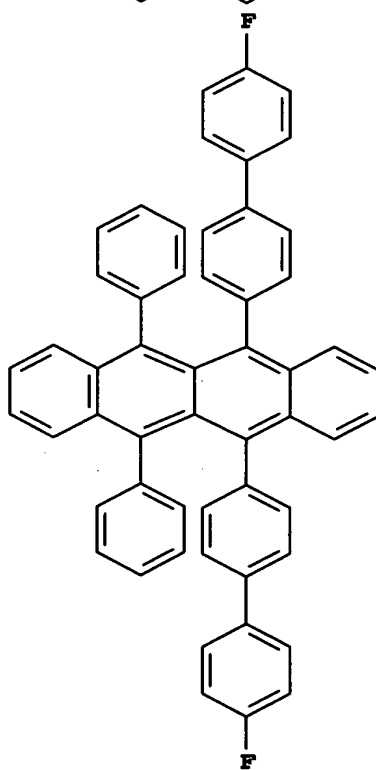
Inv-6



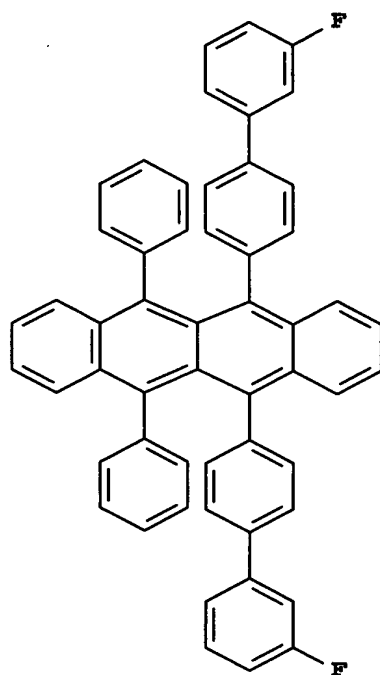
Inv-7



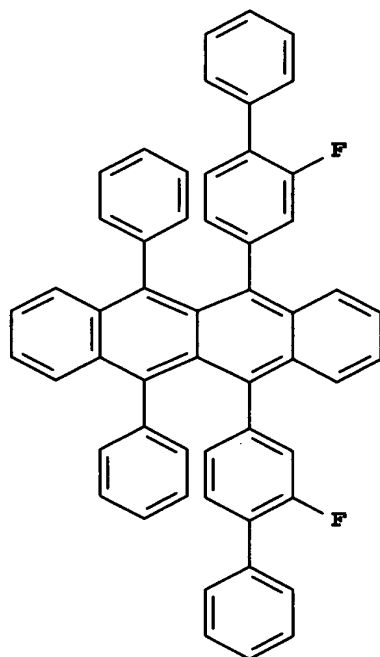
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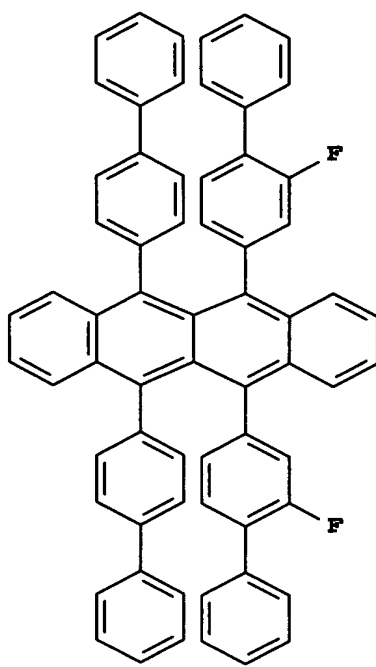
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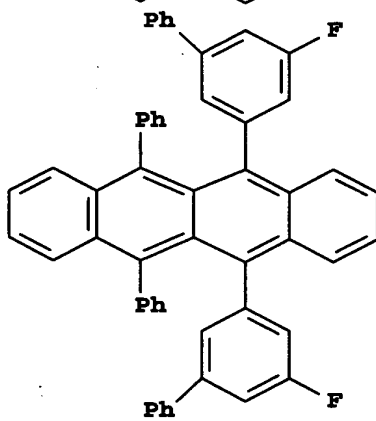
Inv-10



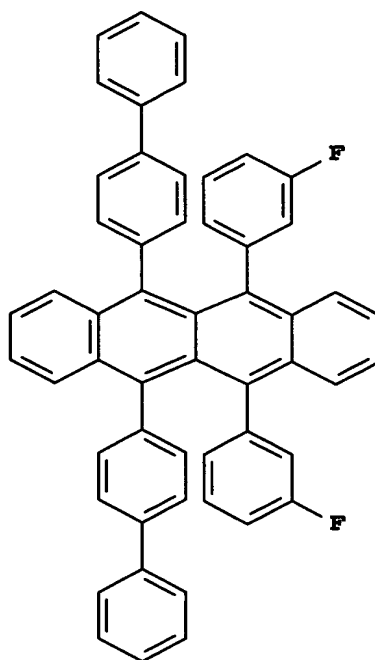
Inv-11



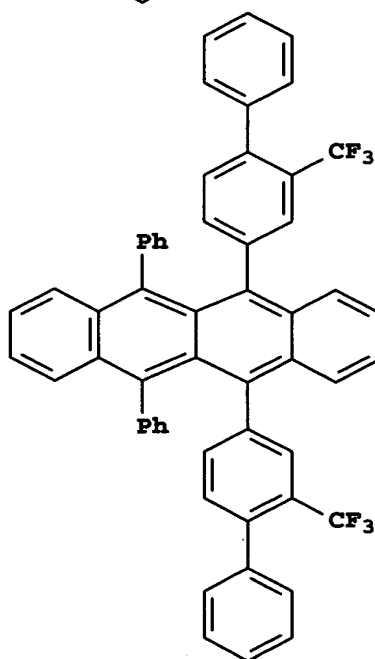
Inv-12



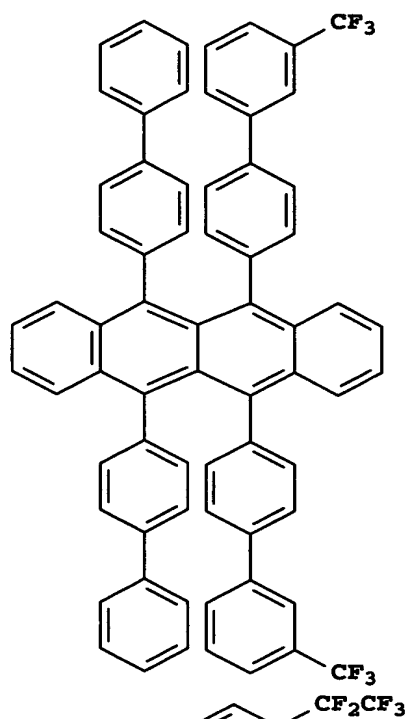
Inv-13



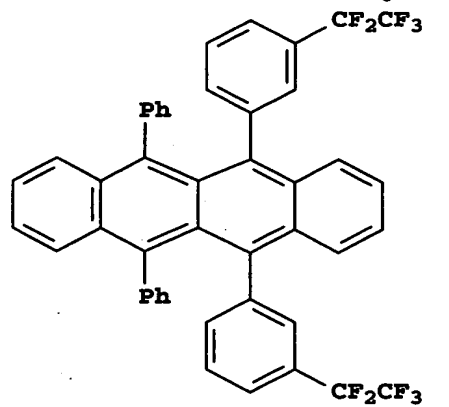
Inv-14



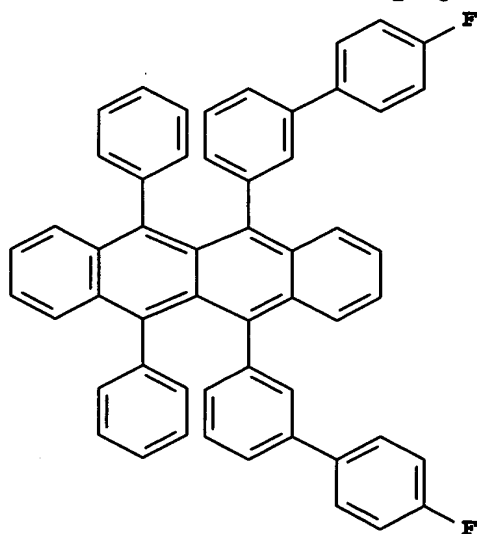
Inv-15



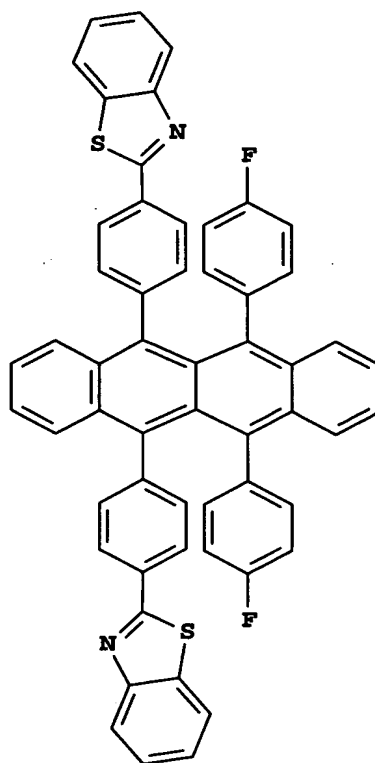
Inv-16



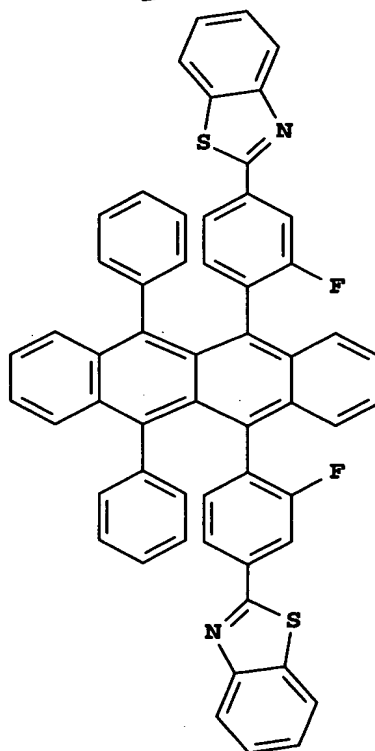
Inv-17



Inv-18



Inv-19



Unless otherwise specifically stated, use of the term "substituted" or "substituent" means any group or atom other than hydrogen. Additionally, when

the term "group" is used, it means that when a substituent group contains a substitutable hydrogen, it is also intended to encompass not only the substituent's unsubstituted form, but also its form further substituted with any substituent group or groups as herein mentioned, so long as the substituent does not destroy

5 properties necessary for device utility. Suitably, a substituent group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous, sulfur, selenium, or boron. The substituent may be, for example, halogen, such as chloro, bromo or fluoro; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl,

10 including straight or branched chain or cyclic alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-*t*-pentylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-*t*-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl,

15 4-*t*-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, *alpha*-(2,4-di-*t*-pentylphenoxy)acetamido, *alpha*-(2,4-di-*t*-pentylphenoxy)butyramido, *alpha*-(3-pentadecylphenoxy)-hexanamido, *alpha*-(4-hydroxy-3-*t*-butylphenoxy)-

20 tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, *N*-methyltetradecanamido, *N*-succinimido, *N*-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and *N*-acetyl-*N*-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-*t*-butylphenoxycarbonylamino,

25 phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecylphenylcarbonylamino, *p*-tolylcarbonylamino, *N*-methylureido, *N,N*-dimethylureido, *N*-methyl-*N*-dodecylureido, *N*-hexadecylureido, *N,N*-dioctadecylureido, *N,N*-dioctyl-*N'*-ethylureido, *N*-phenylureido, *N,N*-diphenylureido, *N*-phenyl-*N*-*p*-tolylureido, *N*-(*m*-hexadecylphenyl)ureido, *N,N*-

30 (2,5-di-*t*-pentylphenyl)-*N'*-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-tolylsulfonamido, *p*-

dodecylbenzenesulfonamido, *N*-methyltetradecylsulfonamido, *N,N*-dipropylsulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as *N*-methylsulfamoyl, *N*-ethylsulfamoyl, *N,N*-dipropylsulfamoyl, *N*-hexadecylsulfamoyl, *N,N*-dimethylsulfamoyl, *N*-[3-(dodecyloxy)propyl]sulfamoyl, 5 *N*-[4-(2,4-di-*t*-pentylphenoxy)butyl]sulfamoyl, *N*-methyl-*N*-tetradecylsulfamoyl, and *N*-dodecylsulfamoyl; carbamoyl, such as *N*-methylcarbamoyl, *N,N*-dibutylcarbamoyl, *N*-octadecylcarbamoyl, *N*-[4-(2,4-di-*t*-pentylphenoxy)butyl]carbamoyl, *N*-methyl-*N*-tetradecylcarbamoyl, and *N,N*-dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl, 10 phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxycarbonyl, and dodecyloxycarbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl, 15 methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-tolylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-tolylsulfinyl; thio, 20 such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-*t*-octylphenylthio, and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamidobenzoyloxy, *N*-phenylcarbamoyloxy, *N*-ethylcarbamoyloxy, and cyclohexylcarbonyloxy; amine, such as phenylanilino, 2-chloroanilino, 25 diethylamine, dodecylamine; imino, such as 1 (*N*-phenylimido)ethyl, *N*-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring 30 composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen, sulfur, phosphorous, or boron. such as 2-furyl, 2-

thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; quaternary phosphonium, such as triphenylphosphonium; and silyloxy, such as trimethylsilyloxy.

If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired desirable properties for a specific application and can include, for example, electron-withdrawing groups, electron-donating groups, and steric groups. When a molecule may have two or more substituents, the substituents may be joined together to form a ring such as a fused ring unless otherwise provided. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

General Device Architecture

The present invention can be employed in many EL device configurations using small molecule materials, oligomeric materials, polymeric materials, or combinations thereof. These include very simple structures comprising a single anode and cathode to more complex devices, such as passive matrix displays comprised of orthogonal arrays of anodes and cathodes to form pixels, and active-matrix displays where each pixel is controlled independently, for example, with thin film transistors (TFTs).

There are numerous configurations of the organic layers wherein the present invention can be successfully practiced. The essential requirements of an OLED are an anode, a cathode, and an organic light-emitting layer located between the anode and cathode. Additional layers may be employed as more fully described hereafter.

A typical structure according to the present invention and especially useful for a small molecule device, is shown in FIG. 1 and is comprised of a substrate 101, an anode 103, a hole-injecting layer 105, a hole-transporting layer 107, a light-emitting layer 109, an electron-transporting layer 111, and a

cathode 113. These layers are described in detail below. Note that the substrate 101 may alternatively be located adjacent to the cathode 113, or the substrate 101 may actually constitute the anode 103 or cathode 113. The organic layers between the anode 103 and cathode 113 are conveniently referred to as the organic EL
5 element. Also, the total combined thickness of the organic layers is desirably less than 500 nm. If the device includes phosphorescent material, a hole-blocking layer, located between the light-emitting layer and the electron-transporting layer, may be present.

The anode 103 and cathode 113 of the OLED are connected to a
10 voltage/current source through electrical conductors. The OLED is operated by applying a potential between the anode 103 and cathode 113 such that the anode 103 is at a more positive potential than the cathode 113. Holes are injected into the organic EL element from the anode 103 and electrons are injected into the organic EL element at the cathode 113. Enhanced device stability can sometimes
15 be achieved when the OLED is operated in an AC mode where, for some time period in the AC cycle, the potential bias is reversed and no current flows. An example of an AC driven OLED is described in US 5,552,678.

Substrate

The OLED device of this invention is typically provided over a
20 supporting substrate 101 where either the cathode 113 or anode 103 can be in contact with the substrate. The electrode in contact with the substrate 101 is conveniently referred to as the bottom electrode. Conventionally, the bottom electrode is the anode 103, but this invention is not limited to that configuration. The substrate 101 can either be light transmissive or opaque, depending on the
25 intended direction of light emission. The light transmissive property is desirable for viewing the EL emission through the substrate 101. Transparent glass or plastic is commonly employed in such cases. The substrate 101 can be a complex structure comprising multiple layers of materials. This is typically the case for active matrix substrates wherein TFTs are provided below the OLED layers. It is
30 still necessary that the substrate 101, at least in the emissive pixelated areas, be comprised of largely transparent materials such as glass or polymers. For

applications where the EL emission is viewed through the top electrode, the transmissive characteristic of the bottom support is immaterial, and therefore the substrate can be light transmissive, light absorbing or light reflective. Substrates for use in this case include, but are not limited to, glass, plastic, semiconductor materials such as silicon, ceramics, and circuit board materials. Again, the substrate **101** can be a complex structure comprising multiple layers of materials such as found in active matrix TFT designs. It is necessary to provide in these device configurations a light-transparent top electrode.

Anode

When the desired electroluminescent light emission (EL) is viewed through the anode, the anode **103** should be transparent or substantially transparent to the emission of interest. Common transparent anode materials used in this invention are indium-tin oxide (ITO), indium-zinc oxide (IZO) and tin oxide, but other metal oxides can work including, but not limited to, aluminum- or indium-doped zinc oxide, magnesium-indium oxide, and nickel-tungsten oxide. In addition to these oxides, metal nitrides, such as gallium nitride, and metal selenides, such as zinc selenide, and metal sulfides, such as zinc sulfide, can be used as the anode **103**. For applications where EL emission is viewed only through the cathode **113**, the transmissive characteristics of the anode **103** are immaterial and any conductive material can be used, transparent, opaque or reflective. Example conductors for this application include, but are not limited to, gold, iridium, molybdenum, palladium, and platinum. Typical anode materials, transmissive or otherwise, have a work function of 4.1 eV or greater. Desired anode materials are commonly deposited by any suitable means such as evaporation, sputtering, chemical vapor deposition, or electrochemical means. Anodes can be patterned using well-known photolithographic processes. Optionally, anodes may be polished prior to application of other layers to reduce surface roughness so as to minimize short circuits or enhance reflectivity.

Cathode

When light emission is viewed solely through the anode **103**, the cathode **113** used in this invention can be comprised of nearly any conductive material. Desirable materials have good film-forming properties to ensure good

contact with the underlying organic layer, promote electron injection at low voltage, and have good stability. Useful cathode materials often contain a low work function metal (< 4.0 eV) or metal alloy. One useful cathode material is comprised of a Mg:Ag alloy wherein the percentage of silver is in the range of 1 to 20 %, as described in U.S. Patent No. 4,885,221. Another suitable class of cathode materials includes bilayers comprising the cathode and a thin electron-injection layer (EIL) in contact with an organic layer (e.g., an electron transporting layer (ETL)), the cathode being capped with a thicker layer of a conductive metal. Here, the EIL preferably includes a low work function metal or metal salt, and if so, the thicker capping layer does not need to have a low work function. One such cathode is comprised of a thin layer of LiF followed by a thicker layer of Al as described in U.S. Patent No. 5,677,572. An ETL material doped with an alkali metal, for example, Li-doped Alq, is another example of a useful EIL. Other useful cathode material sets include, but are not limited to, those disclosed in U.S. Patent Nos. 5,059,861, 5,059,862, and 6,140,763.

When light emission is viewed through the cathode, the cathode must be transparent or nearly transparent. For such applications, metals must be thin or one must use transparent conductive oxides, or a combination of these materials. Optically transparent cathodes have been described in more detail in US 4,885,211, US 5,247,190, JP 3,234,963, US 5,703,436, US 5,608,287, US 5,837,391, US 5,677,572, US 5,776,622, US 5,776,623, US 5,714,838, US 5,969,474, US 5,739,545, US 5,981,306, US 6,137,223, US 6,140,763, US 6,172,459, EP 1 076 368, US 6,278,236, and US 6,284,3936. Cathode materials are typically deposited by any suitable method such as evaporation, sputtering, or chemical vapor deposition. When needed, patterning can be achieved through many well known methods including, but not limited to, through-mask deposition, integral shadow masking as described in US 5,276,380 and EP 0 732 868, laser ablation, and selective chemical vapor deposition.

Hole-Injecting Layer (HIL)

A hole-injecting layer 105 may be provided between anode 103 and hole-transporting layer 107. The hole-injecting layer can serve to improve the film

formation property of subsequent organic layers and to facilitate injection of holes into the hole-transporting layer 107. Suitable materials for use in the hole-injecting layer 105 include, but are not limited to, porphyrinic compounds as described in US 4,720,432, plasma-deposited fluorocarbon polymers as described in US 6,208,075, and some aromatic amines, for example, MTDATA (4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine). Alternative hole-injecting materials reportedly useful in organic EL devices are described in EP 0 891 121 A1 and EP 1 029 909 A1. A hole-injection layer is conveniently used in the present invention, and is desirably a plasma-deposited fluorocarbon polymer. The thickness of a hole-injection layer containing a plasma-deposited fluorocarbon polymer can be in the range of 0.2 nm to 15 nm and suitably in the range of 0.3 to 1.5 nm.

Hole-Transporting Layer (HTL)

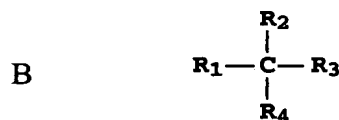
While not always necessary, it is often useful to include a hole-transporting layer in an OLED device. The hole-transporting layer 107 of the organic EL device contains at least one hole-transporting compound such as an aromatic tertiary amine, where the latter is understood to be a compound containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylamine are illustrated by Klupfel et al. US 3,180,730. Other suitable triarylamine substituted with one or more vinyl radicals and/or comprising at least one active hydrogen containing group are disclosed by Brantley et al US 3,567,450 and US 3,658,520.

A more preferred class of aromatic tertiary amines is those which include at least two aromatic tertiary amine moieties as described in US 4,720,432 and US 5,061,569. Such compounds include those represented by structural formula (A).



wherein Q₁ and Q₂ are independently selected aromatic tertiary amine moieties and G is a linking group such as an arylene, cycloalkylene, or alkylene group of a carbon to carbon bond. In one embodiment, at least one of Q₁ or Q₂ contains a polycyclic fused ring structure, e.g., a naphthalene. When G is an aryl group, it is
 5 conveniently a phenylene, biphenylene, or naphthalene moiety.

A useful class of triarylamines satisfying structural formula (A) and containing two triarylamine moieties is represented by structural formula (B):



where

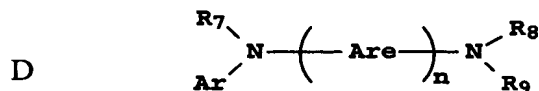
R₁ and R₂ each independently represents a hydrogen atom, an aryl group,
 10 or an alkyl group or R₁ and R₂ together represent the atoms completing a cycloalkyl group; and

R₃ and R₄ each independently represents an aryl group, which is in turn substituted with a diaryl substituted amino group, as indicated by structural formula (C):



15 wherein R₅ and R₆ are independently selected aryl groups. In one embodiment, at least one of R₅ or R₆ contains a polycyclic fused ring structure, e.g., a naphthalene.

Another class of aromatic tertiary amines is the tetraaryldiamines. Desirable tetraaryldiamines include two diarylamino groups, such as indicated by formula (C), linked through an arylene group. Useful tetraaryldiamines include
 20 those represented by formula (D).



wherein

each Are is an independently selected arylene group, such as a phenylene or anthracene moiety,

n is an integer of from 1 to 4, and

Ar, R₇, R₈, and R₉ are independently selected aryl groups.

In a typical embodiment, at least one of Ar, R₇, R₈, and R₉ is a polycyclic fused ring structure, e.g., a naphthalene.

5 The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural formulae (A), (B), (C), (D), can each in turn be substituted. Typical substituents include alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halide such as fluoride, chloride, and bromide. The various alkyl and alkylene moieties typically contain from about 1 to 6 carbon atoms. The
10 cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or seven ring carbon atoms--e.g., cyclopentyl, cyclohexyl, and cycloheptyl ring structures. The aryl and arylene moieties are usually phenyl and phenylene moieties.

 The hole-transporting layer can be formed of a single tertiary amine
15 compound or a mixture of such compounds. Specifically, one may employ a triarylamine, such as a triarylamine satisfying the formula (B), in combination with a tetraaryldiamine, such as indicated by formula (D). Illustrative of useful aromatic tertiary amines are the following:

 1,1-Bis(4-di-*p*-tolylaminophenyl)cyclohexane (TAPC)
20 1,1-Bis(4-di-*p*-tolylaminophenyl)-4-methylcyclohexane
 1,1-Bis(4-di-*p*-tolylaminophenyl)-4-phenylcyclohexane
 1,1-Bis(4-di-*p*-tolylaminophenyl)-3-phenylpropane (TAPPP)
 N,N,N',N'-tetraphenyl-4,4'''-diamino-1,1':4',1'':4'',1'''-quaterphenyl
 Bis(4-dimethylamino-2-methylphenyl)phenylmethane
25 1,4-bis[2-[4-[*N,N*-di(*p*-tolyl)amino]phenyl]vinyl]benzene (BDTAPVB)
 N,N,N',N'-Tetra-*p*-tolyl-4,4'-diaminobiphenyl (TTB)
 N,N,N',N'-Tetraphenyl-4,4'-diaminobiphenyl
 N,N,N',N'-tetra-1-naphthyl-4,4'-diaminobiphenyl
 N,N,N',N'-tetra-2-naphthyl-4,4'-diaminobiphenyl
30 *N*-Phenylcarbazole
 4,4'-Bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB)

4,4'-Bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]biphenyl (TNB)
 4,4'-Bis[*N*-(1-naphthyl)-*N*-phenylamino]*p*-terphenyl
 4,4'-Bis[*N*-(2-naphthyl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(3-acenaphthenyl)-*N*-phenylamino]biphenyl
 5 1,5-Bis[*N*-(1-naphthyl)-*N*-phenylamino]naphthalene
 4,4'-Bis[*N*-(9-anthryl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(1-anthryl)-*N*-phenylamino]-*p*-terphenyl
 4,4'-Bis[*N*-(2-phenanthryl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(8-fluoranthenyl)-*N*-phenylamino]biphenyl
 10 4,4'-Bis[*N*-(2-pyrenyl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(2-naphthacenyl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(2-perylenyl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(1-coronenyl)-*N*-phenylamino]biphenyl
 2,6-Bis(di-*p*-tolylamino)naphthalene
 15 2,6-Bis[di-(1-naphthyl)amino]naphthalene
 2,6-Bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]naphthalene
N,N,N',N'-Tetra(2-naphthyl)-4,4''-diamino-*p*-terphenyl
 4,4'-Bis{*N*-phenyl-*N*-[4-(1-naphthyl)-phenyl]amino}biphenyl
 2,6-Bis[*N,N*-di(2-naphthyl)amino]fluorene
 20 4,4',4''-tris[(3-methylphenyl)phenylamino]triphenylamine (MTDATA)
 4,4'-Bis[*N*-(3-methylphenyl)-*N*-phenylamino]biphenyl (TPD)

Another class of useful hole-transporting materials includes polycyclic aromatic compounds as described in EP 1 009 041. Tertiary aromatic amines with more than two amine groups may be used including oligomeric
 25 materials. In addition, polymeric hole-transporting materials can be used such as poly(*N*-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, and copolymers such as poly(3,4-ethylenedioxythiophene) / poly(4-styrenesulfonate) also called PEDOT/PSS. It is also possible for the hole-transporting layer to comprise two or more sublayers of differing compositions, the composition of
 30 each sublayer being as described above. The thickness of the hole-transporting layer can be between 10 and about 500 nm and suitably between 50 and 300 nm.

Light-Emitting Layer (LEL)

In addition to the light-emitting materials of this invention, additional light emitting materials may be used in the EL device, including other fluorescent materials. Other fluorescent materials may be used in the same layer as the boron complex material, in adjacent layers, in adjacent pixels, or any combination.

As more fully described in U.S. Patent Nos. 4,769,292 and 5,935,721, the light-emitting layer (LEL) of the organic EL element includes a luminescent material where electroluminescence is produced as a result of electron-hole pair recombination. The light-emitting layer can be comprised of a single material, but more commonly consists of a host material doped with a guest emitting material or materials where light emission comes primarily from the emitting materials and can be of any color. The host materials in the light-emitting layer can be an electron-transporting material, as defined below, a hole-transporting material, as defined above, or another material or combination of materials that support hole-electron recombination. Fluorescent emitting materials are typically incorporated at 0.01 to 10 % by weight of the host material.

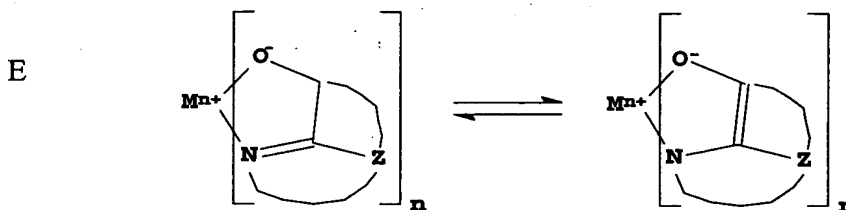
The host and emitting materials can be small non-polymeric molecules or polymeric materials such as polyfluorenes and polyvinylarylenes (e.g., poly(*p*-phenylenevinylene), PPV). In the case of polymers, small-molecule emitting materials can be molecularly dispersed into a polymeric host, or the emitting materials can be added by copolymerizing a minor constituent into a host polymer. Host materials may be mixed together in order to improve film formation, electrical properties, light emission efficiency, operating lifetime, or manufacturability. The host may comprise a material that has good hole-transporting properties and a material that has good electron-transporting properties.

An important relationship for choosing a fluorescent material as a guest emitting material is a comparison of the excited singlet-state energies of the host and the fluorescent material. It is highly desirable that the excited singlet-state energy of the fluorescent material be lower than that of the host material.

The excited singlet-state energy is defined as the difference in energy between the emitting singlet state and the ground state. For non-emissive hosts, the lowest excited state of the same electronic spin as the ground state is considered the emitting state.

5 Host and emitting materials known to be of use include, but are not limited to, those disclosed in US 4,768,292, US 5,141,671, US 5,150,006, US 5,151,629, US 5,405,709, US 5,484,922, US 5,593,788, US 5,645,948, US 5,683,823, US 5,755,999, US 5,928,802, US 5,935,720, US 5,935,721, and US 6,020,078.

10 Metal complexes of 8-hydroxyquinoline and similar derivatives, also known as metal-chelated oxinoid compounds (Formula E), constitute one class of useful host compounds capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 500 nm, e.g., green, yellow, orange, and red.



15 wherein

M represents a metal;

n is an integer of from 1 to 4; and

Z independently in each occurrence represents the atoms completing a nucleus having at least two fused aromatic rings.

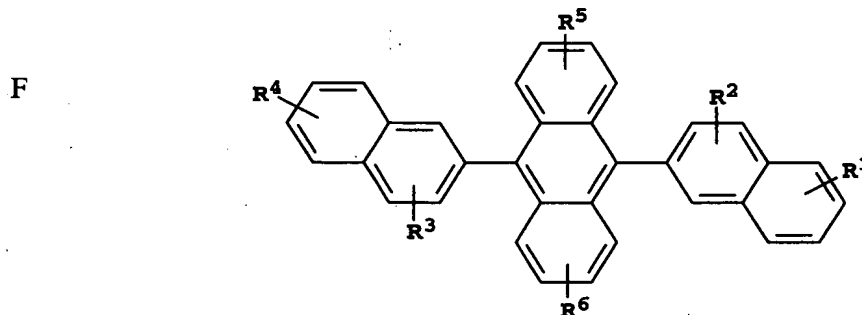
20 From the foregoing it is apparent that the metal can be monovalent, divalent, trivalent, or tetravalent metal. The metal can, for example, be an alkali metal, such as lithium, sodium, or potassium; an alkaline earth metal, such as magnesium or calcium; a trivalent metal, such aluminum or gallium, or another metal such as zinc or zirconium. Generally any monovalent, divalent, trivalent, or
25 tetravalent metal known to be a useful chelating metal can be employed.

Z completes a heterocyclic nucleus containing at least two fused aromatic rings, at least one of which is an azole or azine ring. Additional rings, including both aliphatic and aromatic rings, can be fused with the two required rings, if required. To avoid adding molecular bulk without improving on function
5 the number of ring atoms is usually maintained at 18 or less.

Illustrative of useful chelated oxinoid compounds are the following:

- CO-1: Aluminum trisoxine [alias, tris(8-quinolinolato)aluminum(III)]
CO-2: Magnesium bisoxine [alias, bis(8-quinolinolato)magnesium(II)]
10 CO-3: Bis[benzo {f}-8-quinolinolato]zinc (II)
CO-4: Bis(2-methyl-8-quinolinolato)aluminum(III)-μ-oxo-bis(2-methyl-8-quinolinolato) aluminum(III)
CO-5: Indium trisoxine [alias, tris(8-quinolinolato)indium]
CO-6: Aluminum tris(5-methyloxine) [alias, tris(5-methyl-8-quinolinolato)
15 aluminum(III)]
CO-7: Lithium oxine [alias, (8-quinolinolato)lithium(I)]
CO-8: Gallium oxine [alias, tris(8-quinolinolato)gallium(III)]
CO-9: Zirconium oxine [alias, tetra(8-quinolinolato)zirconium(IV)]

Derivatives of 9,10-di-(2-naphthyl)anthracene (Formula F)
20 constitute one class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g., blue, green, yellow, orange or red.



wherein: R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 represent one or more substituents on each ring where each substituent is individually selected from the following groups:

Group 1: hydrogen, or alkyl of from 1 to 24 carbon atoms;

Group 2: aryl or substituted aryl of from 5 to 20 carbon atoms;

5 Group 3: carbon atoms from 4 to 24 necessary to complete a fused aromatic ring of anthracenyl; pyrenyl, or perylenyl;

Group 4: heteroaryl or substituted heteroaryl of from 5 to 24 carbon atoms as necessary to complete a fused heteroaromatic ring of furyl, thienyl, pyridyl, quinolinyl or other heterocyclic systems;

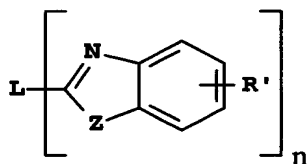
10 Group 5: alkoxyamino, alkylamino, or arylamino of from 1 to 24 carbon atoms; and

Group 6: fluorine, chlorine, bromine or cyano.

Illustrative examples include 9,10-di-(2-naphthyl)anthracene and 2-*t*-butyl-9,10-di-(2-naphthyl)anthracene. Other anthracene derivatives can be useful
15 as a host in the LEL, including derivatives of 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene.

Benzazole derivatives (Formula G) constitute another class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g.,
20 blue, green, yellow, orange or red.

G



wherein:

n is an integer of 3 to 8;

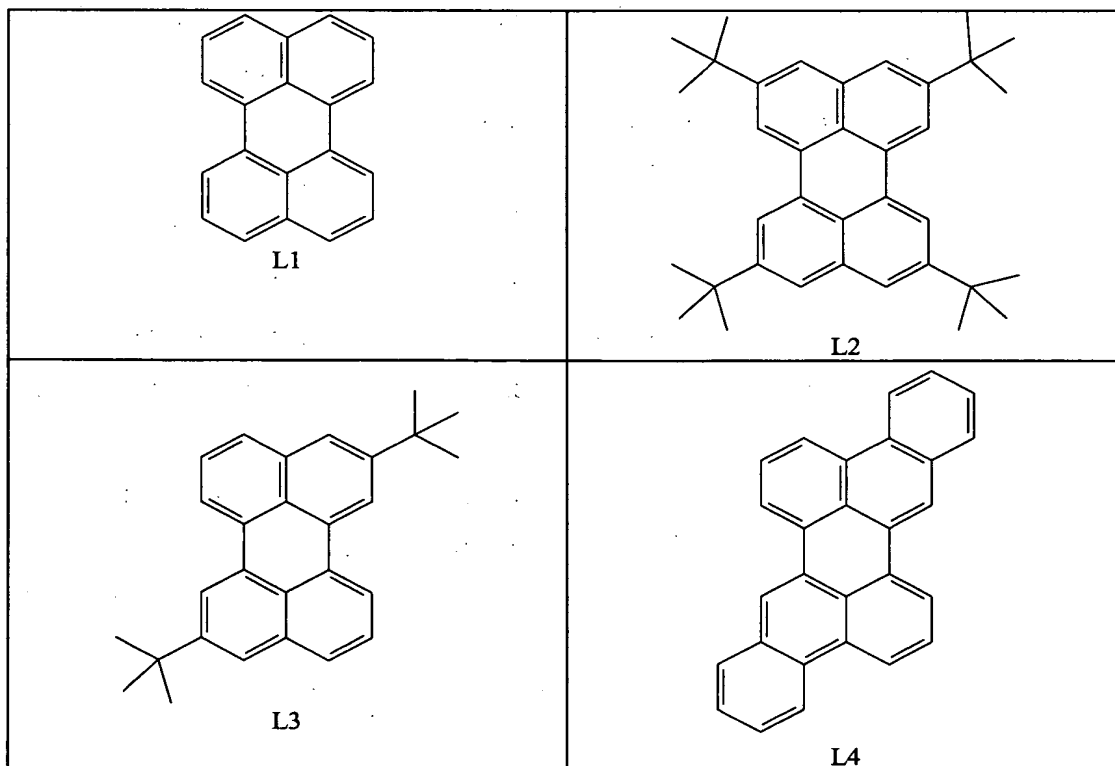
Z is O, NR or S; and

R and R' are individually hydrogen; alkyl of from 1 to 24 carbon atoms, for example, propyl, *t*-butyl, heptyl, and the like; aryl or hetero-atom substituted
25 aryl of from 5 to 20 carbon atoms for example phenyl and naphthyl, furyl, thienyl, pyridyl, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring; and

L is a linkage unit consisting of alkyl, aryl, substituted alkyl, or substituted aryl, which connects the multiple benzazoles together. L may be either conjugated with the multiple benzazoles or not in conjugation with them. An example of a useful benzazole is 2,2',2''-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole].

5 Styrylarylene derivatives as described in U.S. Patent 5,121,029 and JP 08333569 are also useful hosts for blue emission. For example, 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene and 4,4'-bis(2,2-diphenylethenyl)-1,1'-biphenyl (DPVBi) are useful hosts for blue emission.

Useful fluorescent emitting materials include, but are not limited to, derivatives of anthracene, tetracene, xanthene, perylene, rubrene, coumarin, rhodamine, and quinacridone, dicyanomethylenepyran compounds, thiopyran compounds, polymethine compounds, pyrylium and thiapyrylium compounds, fluorene derivatives, perflanthene derivatives, indenoperylene derivatives, bis(azinyl)amine boron compounds, bis(azinyl)methane compounds, and
15 carbostyryl compounds. Illustrative examples of useful materials include, but are not limited to, the following:



L5

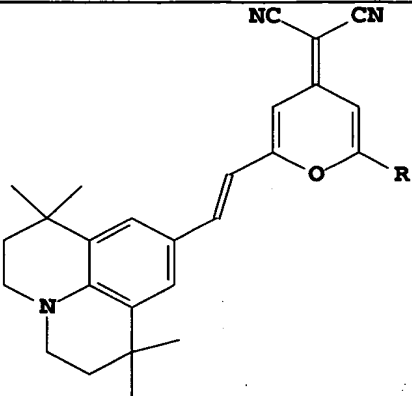
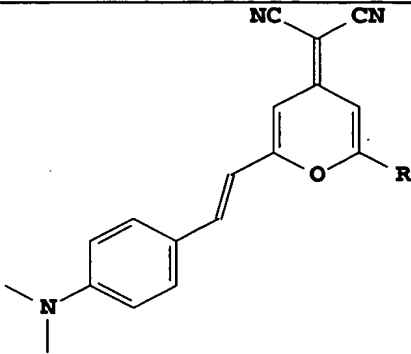
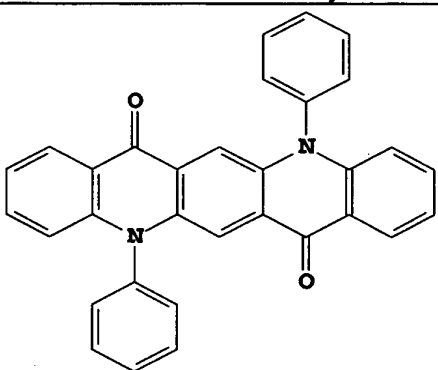
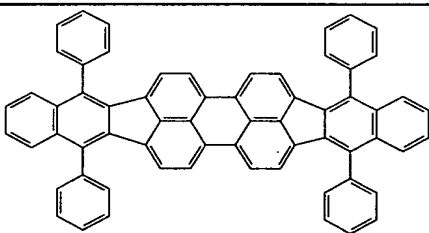
L6

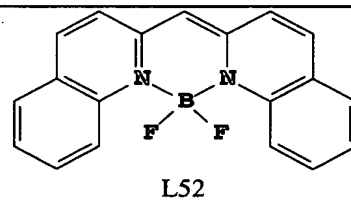
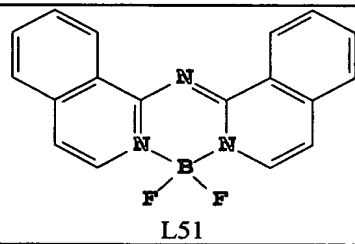
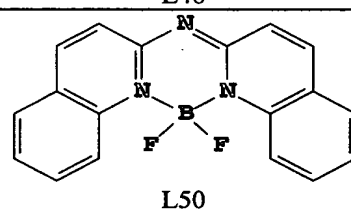
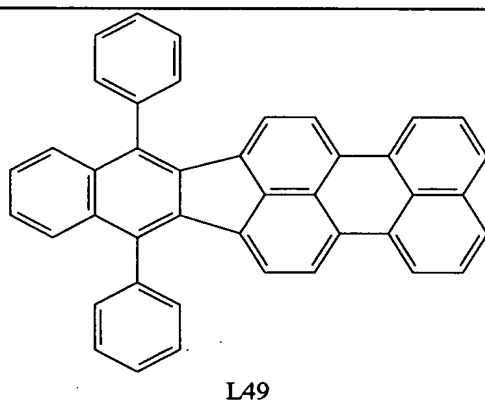
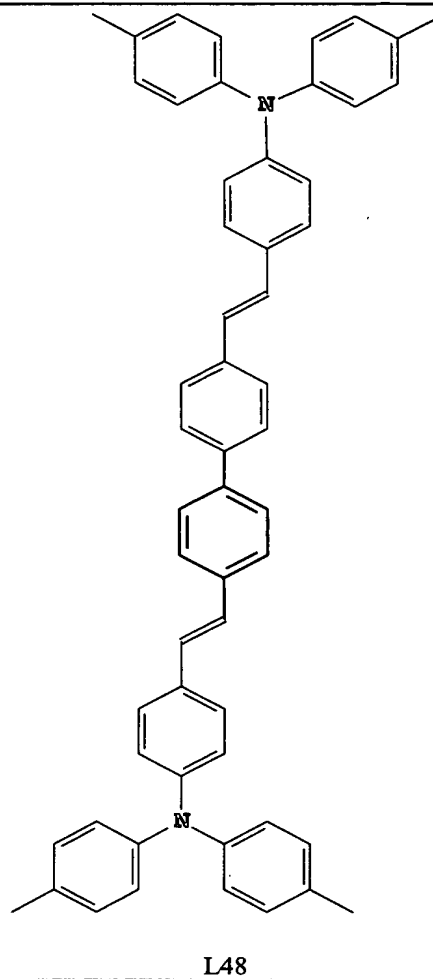
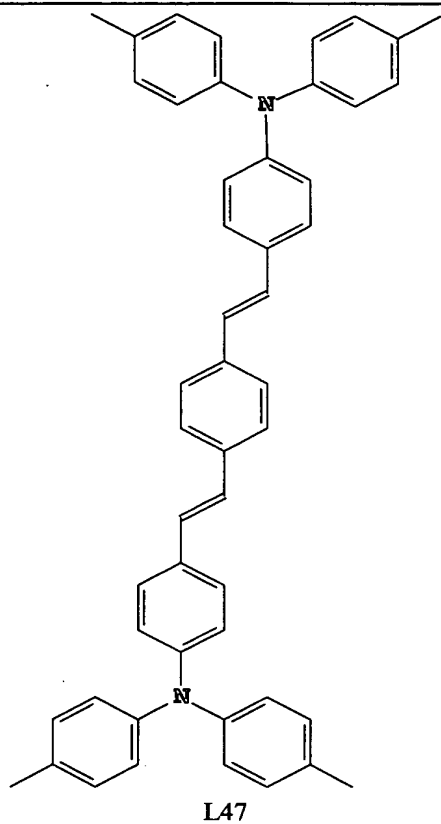
L7

L8

	<u>X</u>	<u>R1</u>	<u>R2</u>
L9	O	H	H
L10	O	H	Methyl
L11	O	Methyl	H
L12	O	Methyl	Methyl
L13	O	H	<i>t</i> -butyl
L14	O	<i>t</i> -butyl	H
L15	O	<i>t</i> -butyl	<i>t</i> -butyl
L16	S	H	H
L17	S	H	Methyl
L18	S	Methyl	H
L19	S	Methyl	Methyl
L20	S	H	<i>t</i> -butyl
L21	S	<i>t</i> -butyl	H
L22	S	<i>t</i> -butyl	<i>t</i> -butyl

	<u>X</u>	<u>R1</u>	<u>R2</u>
L23	O	H	H
L24	O	H	Methyl
L25	O	Methyl	H
L26	O	Methyl	Methyl
L27	O	H	<i>t</i> -butyl
L28	O	<i>t</i> -butyl	H
L29	O	<i>t</i> -butyl	<i>t</i> -butyl
L30	S	H	H
L31	S	H	Methyl
L32	S	Methyl	H
L33	S	Methyl	Methyl
L34	S	H	<i>t</i> -butyl
L35	S	<i>t</i> -butyl	H
L36	S	<i>t</i> -butyl	<i>t</i> -butyl

 <p> L37 L38 L39 L40 </p> <p> <u>R</u> phenyl methyl <i>t</i>-butyl mesityl </p>	 <p> L41 L42 L43 L44 </p> <p> <u>R</u> phenyl methyl <i>t</i>-butyl mesityl </p>
 <p>L45</p>	 <p>L46</p>



In addition to the light-emitting materials of this invention, light-emitting phosphorescent materials may be used in the EL device. For convenience, the phosphorescent complex guest material may be referred to herein as a phosphorescent material. The phosphorescent material typically includes one or more ligands, for example monoanionic ligands that can be coordinated to a metal through an sp^2 carbon and a heteroatom. Conveniently, the ligand can be phenylpyridine (ppy) or derivatives or analogs thereof. Examples of some useful phosphorescent organometallic materials include tris(2-phenylpyridinato-*N,C*^{2'})iridium(III), bis(2-phenylpyridinato-*N,C*^{2'})iridium(III)(acetylacetonate), and bis(2-phenylpyridinato-*N,C*^{2'})platinum(II). Usefully, many phosphorescent organometallic materials emit in the green region of the spectrum, that is, with a maximum emission in the range of 510 to 570 nm.

Phosphorescent materials may be used singly or in combinations with other phosphorescent materials, either in the same or different layers.

Phosphorescent materials and suitable hosts are described in WO 00/57676, WO 00/70655, WO 01/41512 A1, WO 02/15645 A1, US 2003/0017361 A1, WO 01/93642 A1, WO 01/39234 A2, US 6,458,475 B1, WO 02/071813 A1, US 6,573,651 B2, US 2002/0197511 A1, WO 02/074015 A2, US 6,451,455 B1, US 2003/0072964 A1, US 2003/0068528 A1, US 6,413,656 B1, US 6,515,298 B2, US 6,451,415 B1, US 6,097,147, US 2003/0124381 A1, US 2003/0059646 A1, US 2003/0054198 A1, EP 1 239 526 A2, EP 1 238 981 A2, EP 1 244 155 A2, US 2002/0100906 A1, US 2003/0068526 A1, US 2003/0068535 A1, JP 2003073387A, JP 2003 073388A, US 2003/0141809 A1, US 2003/0040627 A1, JP 2003059667A, JP 2003073665A, and US 2002/0121638 A1.

The emission wavelengths of cyclometallated Ir(III) complexes of the type IrL_3 and IrL_2L' , such as the green-emitting *fac*-tris(2-phenylpyridinato-*N,C*^{2'})iridium(III) and bis(2-phenylpyridinato-*N,C*^{2'})iridium(III)(acetylacetonate) may be shifted by substitution of electron donating or withdrawing groups at appropriate positions on the cyclometallating ligand L, or by choice of different heterocycles for the cyclometallating ligand L. The emission wavelengths may also be shifted by choice of the ancillary ligand L'. Examples of red emitters are

the bis(2-(2'-benzothienyl)pyridinato-*N,C*^{3'})iridium(III)(acetylacetonate) and tris(2-phenylisoquinolino-*N,C*)iridium(III). A blue-emitting example is bis(2-(4,6-difluorophenyl)-pyridinato-*N,C*^{2'})iridium(III)(picolinate).

Red electrophosphorescence has been reported, using bis(2-(2'-benzo[4,5-a]thienyl)pyridinato-*N,C*^{3'}) iridium (acetylacetonate) [Btp₂Ir(acac)] as the phosphorescent material (C. Adachi, S. Lamansky, M. A. Baldo, R. C. Kwong, M. E. Thompson, and S. R. Forrest, *App. Phys. Lett.*, **78**, 1622-1624 (2001)).

Other important phosphorescent materials include cyclometallated Pt(II) complexes such as cis-bis(2-phenylpyridinato-*N,C*^{2'})platinum(II), cis-bis(2-(2'-thienyl)pyridinato-*N,C*^{3'}) platinum(II), cis-bis(2-(2'-thienyl)quinolino-*N,C*^{5'}) platinum(II), or (2-(4,6-difluorophenyl)pyridinato-*N,C*^{2'}) platinum (II) (acetylacetonate). Pt (II) porphyrin complexes such as 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphine platinum(II) are also useful phosphorescent materials.

Still other examples of useful phosphorescent materials include coordination complexes of the trivalent lanthanides such as Tb³⁺ and Eu³⁺ (J. Kido et al., *Appl. Phys. Lett.*, **65**, 2124 (1994)).

Suitable host materials for phosphorescent materials should be selected so that transfer of a triplet exciton can occur efficiently from the host material to the phosphorescent material but cannot occur efficiently from the phosphorescent material to the host material. Therefore, it is highly desirable that the triplet energy of the phosphorescent material be lower than the triplet energy of the host. Generally speaking, a large triplet energy implies a large optical bandgap. However, the band gap of the host should not be chosen so large as to cause an unacceptable barrier to injection of charge carriers into the light-emitting layer and an unacceptable increase in the drive voltage of the OLED. Suitable host materials are described in WO 00/70655 A2; 01/39234 A2; 01/ 93642 A1; 02/074015 A2; 02/15645 A1, and US 20020117662. Suitable hosts include certain aryl amines, triazoles, indoles and carbazole compounds. Examples of desirable hosts are 4,4'-*N,N'*-dicarbazole-biphenyl, otherwise known as 4,4'-bis(carbazol-9-yl)biphenyl or CBP; 4,4'-*N,N'*-dicarbazole-2,2'-dimethyl-biphenyl, otherwise known as 2,2'-

dimethyl-4,4'-bis(carbazol-9-yl)biphenyl or CDBP; 1,3-bis(*N,N'*-dicarbazole)benzene, otherwise known as 1,3-bis(carbazol-9-yl)benzene, and poly(*N*-vinylcarbazole), including their derivatives.

Desirable host materials are capable of forming a continuous film.

5 Hole-Blocking Layer (HBL)

In addition to suitable hosts, an OLED device employing a phosphorescent material often requires at least one hole-blocking layer placed between the electron-transporting layer 111 and the light-emitting layer 109 to help confine the excitons and recombination events to the light-emitting layer comprising the host and phosphorescent material. In this case, there should be an energy barrier for hole migration from the host into the hole-blocking layer, while electrons should pass readily from the hole-blocking layer into the light-emitting layer comprising a host and a phosphorescent material. The first requirement entails that the ionization potential of the hole-blocking layer be larger than that of the light-emitting layer 109, desirably by 0.2 eV or more. The second requirement entails that the electron affinity of the hole-blocking layer not greatly exceed that of the light-emitting layer 109, and desirably be either less than that of light-emitting layer or not exceed that of the light-emitting layer by more than about 0.2 eV.

20 When used with an electron-transporting layer whose characteristic luminescence is green, such as an Alq-containing electron-transporting layer as described below, the requirements concerning the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the material of the hole-blocking layer frequently result in a characteristic luminescence of the hole-blocking layer at shorter wavelengths than that of the electron-transporting layer, such as blue, violet, or ultraviolet luminescence. Thus, it is desirable that the characteristic luminescence of the material of a hole-blocking layer be blue, violet, or ultraviolet. It is further desirable, but not absolutely required, that the triplet energy of the hole-blocking material be greater than that of the phosphorescent material. Suitable hole-blocking materials are described in WO 00/70655A2 and WO 01/93642 A1. Two examples of useful

hole-blocking materials are bathocuproine (BCP) and bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminum(III) (BALq). The characteristic luminescence of BCP is in the ultraviolet, and that of BALq is blue. Metal complexes other than BALq are also known to block holes and excitons as described in US 20030068528. In addition, US 20030175553 A1 describes the use of *fac*-tris(1-phenylpyrazolato-*N,C*^{2'})iridium(III) (Irppz) for this purpose.

When a hole-blocking layer is used, its thickness can be between 2 and 100 nm and suitably between 5 and 10 nm.

Electron-Transporting Layer (ETL)

Desirable thin film-forming materials for use in forming the electron-transporting layer 111 of the organic EL devices of this invention are metal-chelated oxinoid compounds, including chelates of oxine itself (also commonly referred to as 8-quinolinol or 8-hydroxyquinoline). Such compounds help to inject and transport electrons, exhibit high levels of performance, and are readily fabricated in the form of thin films. Exemplary of contemplated oxinoid compounds are those satisfying structural formula (E), previously described.

Other electron-transporting materials suitable for use in the electron-transporting layer 111 include various butadiene derivatives as disclosed in US 4,356,429 and various heterocyclic optical brighteners as described in US 4,539,507. Benzazoles satisfying structural formula (G) are also useful electron transporting materials. Triazines are also known to be useful as electron transporting materials.

If both a hole-blocking layer and an electron-transporting layer 111 are used, electrons should pass readily from the electron-transporting layer 111 into the hole-blocking layer. Therefore, the electron affinity of the electron-transporting layer 111 should not greatly exceed that of the hole-blocking layer. Desirably, the electron affinity of the electron-transporting layer should be less than that of the hole-blocking layer or not exceed it by more than about 0.2 eV.

If an electron-transporting layer is used, its thickness may be between 2 and 100 nm and suitably between 5 and 20 nm.

Other Useful Organic Layers and Device Architecture

In some instances, layers 109 through 111 can optionally be collapsed into a single layer that serves the function of supporting both light emission and electron transportation. The hole-blocking layer, when present, and layer 111 may also be collapsed into a single layer that functions to block holes or excitons, and supports electron transport. It also known in the art that emitting materials may be included in the hole-transporting layer 107. In that case, the hole-transporting material may serve as a host. Multiple materials may be added to one or more layers in order to create a white-emitting OLED, for example, by combining blue- and yellow-emitting materials, cyan- and red-emitting materials, or red-, green-, and blue-emitting materials. White-emitting devices are described, for example, in EP 1 187 235, US 20020025419, EP 1 182 244, US 5,683,823, US 5,503,910, US 5,405,709, and US 5,283,182 and can be equipped with a suitable filter arrangement to produce a color emission.

This invention may be used in so-called stacked device architecture, for example, as taught in US 5,703,436 and US 6,337,492.

Deposition of Organic Layers

The organic materials mentioned above are suitably deposited by any means suitable for the form of the organic materials. In the case of small molecules, they are conveniently deposited through sublimation or evaporation, but can be deposited by other means such as coating from a solvent together with an optional binder to improve film formation. If the material is a polymer, solvent deposition is usually preferred. The material to be deposited by sublimation or evaporation can be vaporized from a sublimator "boat" often comprised of a tantalum material, e.g., as described in US 6,237,529, or can be first coated onto a donor sheet and then sublimed in closer proximity to the substrate. Layers with a mixture of materials can utilize separate sublimator boats or the materials can be pre-mixed and coated from a single boat or donor sheet. Patterned deposition can be achieved using shadow masks, integral shadow masks (US 5,294,870), spatially-defined thermal dye transfer from a donor sheet (US 5,688,551, US 5,851,709 and US 6,066,357) or an inkjet method (US 6,066,357).

Encapsulation

Most OLED devices are sensitive to moisture or oxygen, or both, so they are commonly sealed in an inert atmosphere such as nitrogen or argon, along with a desiccant such as alumina, bauxite, calcium sulfate, clays, silica gel, zeolites, alkaline metal oxides, alkaline earth metal oxides, sulfates, or metal halides and perchlorates. Methods for encapsulation and desiccation include, but are not limited to, those described in U.S. Patent No. 6,226,890. In addition, barrier layers such as SiO_x, Teflon, and alternating inorganic/polymeric layers are known in the art for encapsulation. Any of these methods of sealing or encapsulation and desiccation can be used with the EL devices constructed according to the present invention.

Optical Optimization

OLED devices of this invention can employ various well-known optical effects in order to enhance their emissive properties if desired. This includes optimizing layer thicknesses to yield maximum light transmission, providing dielectric mirror structures, replacing reflective electrodes with light-absorbing electrodes, providing anti-glare or anti-reflection coatings over the display, providing a polarizing medium over the display, or providing colored, neutral density, or color-conversion filters over the display. Filters, polarizers, and anti-glare or anti-reflection coatings may be specifically provided over the EL device or as part of the EL device.

Embodiments of the invention can provide advantageous features such as higher luminous yield, lower drive voltage, and higher power efficiency, or reduced sublimation temperatures. Embodiments of the compounds useful in the invention can provide a wide range of hues including those useful in the emission of white light (directly or through filters to provide multicolor displays). Embodiments of the invention can also provide an area lighting device.

The invention and its advantages can be better appreciated by the following examples. Unless otherwise specifically stated, use of the term "substituted" or "substituent" means any group or atom other than hydrogen. Additionally, when the term "group" is used, it means that when a substituent group contains a substitutable hydrogen, it is also intended to encompass not only

the substituent's unsubstituted form, but also its form further substituted with any substituent group or groups as herein mentioned, so long as the substituent does not destroy properties necessary for device utility. Suitably, a substituent group may be halogen or may be bonded to the remainder of the molecule by an atom of

5 carbon, silicon, oxygen, nitrogen, phosphorous, sulfur, selenium, or boron. The substituent may be, for example, halogen, such as chloro, bromo or fluoro; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain or cyclic alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-*t*-pentylphenoxy) propyl, and tetradecyl;

10 alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-*t*-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-*t*-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as

15 acetamido, benzamido, butyramido, tetradecanamido, *alpha*-(2,4-di-*t*-pentylphenoxy)acetamido, *alpha*-(2,4-di-*t*-pentylphenoxy)butyramido, *alpha*-(3-pentadecylphenoxy)-hexanamido, *alpha*-(4-hydroxy-3-*t*-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, *N*-methyltetradecanamido, *N*-succinimido, *N*-phthalimido, 2,5-dioxo-1-oxazolidinyl,

20 3-dodecyl-2,5-dioxo-1-imidazolyl, and *N*-acetyl-*N*-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-*t*-butylphenoxycarbonylamino, phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecylphenylcarbonylamino, *p*-tolylcarbonylamino, *N*-methylureido, *N,N*-

25 dimethylureido, *N*-methyl-*N*-dodecylureido, *N*-hexadecylureido, *N,N*-dioctadecylureido, *N,N*-dioctyl-*N'*-ethylureido, *N*-phenylureido, *N,N*-diphenylureido, *N*-phenyl-*N*-*p*-tolylureido, *N*-(*m*-hexadecylphenyl)ureido, *N,N*-(2,5-di-*t*-pentylphenyl)-*N'*-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-tolylsulfonamido, *p*-

30 dodecylbenzenesulfonamido, *N*-methyltetradecylsulfonamido, *N,N*-dipropylsulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as *N*-

methylsulfamoyl, *N*-ethylsulfamoyl, *N,N*-dipropylsulfamoyl, *N*-
 hexadecylsulfamoyl, *N,N*-dimethylsulfamoyl, *N*-[3-(dodecyloxy)propyl]sulfamoyl,
N-[4-(2,4-di-*t*-pentylphenoxy)butyl]sulfamoyl, *N*-methyl-*N*-tetradecylsulfamoyl,
 and *N*-dodecylsulfamoyl; carbamoyl, such as *N*-methylcarbamoyl, *N,N*-
 5 dibutylcarbamoyl, *N*-octadecylcarbamoyl, *N*-[4-(2,4-di-*t*-
 pentylphenoxy)butyl]carbamoyl, *N*-methyl-*N*-tetradecylcarbamoyl, and *N,N*-
 dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl,
 phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl methoxycarbonyl,
 butoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-
 10 pentadecyloxycarbonyl, and dodecyloxycarbonyl; sulfonyl, such as
 methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-
 ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl,
 methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl,
 hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-tolylsulfonyl;
 15 sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such
 as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl,
 hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-tolylsulfinyl; thio,
 such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-
 pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-*t*-octylphenylthio, and *p*-
 20 tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-
 dodecylamidobenzoyloxy, *N*-phenylcarbamoyloxy, *N*-ethylcarbamoyloxy, and
 cyclohexylcarbonyloxy; amine, such as phenylanilino, 2-chloroanilino,
 diethylamine, dodecylamine; imino, such as 1 (*N*-phenylimido)ethyl, *N*-
 succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and
 25 ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a
 heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of
 which may be substituted and which contain a 3 to 7 membered heterocyclic ring
 composed of carbon atoms and at least one hetero atom selected from the group
 consisting of oxygen, nitrogen, sulfur, phosphorous, or boron. such as 2-furyl, 2-
 30 thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as

triethylammonium; quaternary phosphonium, such as triphenylphosphonium; and silyloxy, such as trimethylsilyloxy.

If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular
5 substituents used may be selected by those skilled in the art to attain the desired desirable properties for a specific application and can include, for example, electron-withdrawing groups, electron-donating groups, and steric groups. When a molecule may have two or more substituents, the substituents may be joined together to form a ring such as a fused ring unless otherwise provided. Generally,
10 the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

General Device Architecture

15 The present invention can be employed in many EL device configurations using small molecule materials, oligomeric materials, polymeric materials, or combinations thereof. These include very simple structures comprising a single anode and cathode to more complex devices, such as passive matrix displays comprised of orthogonal arrays of anodes and cathodes to form
20 pixels, and active-matrix displays where each pixel is controlled independently, for example, with thin film transistors (TFTs).

There are numerous configurations of the organic layers wherein the present invention can be successfully practiced. The essential requirements of an OLED are an anode, a cathode, and an organic light-emitting layer located
25 between the anode and cathode. Additional layers may be employed as more fully described hereafter.

A typical structure according to the present invention and especially useful for a small molecule device, is shown in FIG. 1 and is comprised of a substrate 101, an anode 103, a hole-injecting layer 105, a hole-transporting
30 layer 107, a light-emitting layer 109, an electron-transporting layer 111, and a cathode 113. These layers are described in detail below. Note that the substrate

101 may alternatively be located adjacent to the cathode 113, or the substrate 101 may actually constitute the anode 103 or cathode 113. The organic layers between the anode 103 and cathode 113 are conveniently referred to as the organic EL element. Also, the total combined thickness of the organic layers is desirably less
5 than 500 nm. If the device includes phosphorescent material, a hole-blocking layer, located between the light-emitting layer and the electron-transporting layer, may be present.

The anode 103 and cathode 113 of the OLED are connected to a voltage/current source through electrical conductors. The OLED is operated by
10 applying a potential between the anode 103 and cathode 113 such that the anode 103 is at a more positive potential than the cathode 113. Holes are injected into the organic EL element from the anode 103 and electrons are injected into the organic EL element at the cathode 113. Enhanced device stability can sometimes be achieved when the OLED is operated in an AC mode where, for some time
15 period in the AC cycle, the potential bias is reversed and no current flows. An example of an AC driven OLED is described in US 5,552,678.

Substrate

The OLED device of this invention is typically provided over a supporting substrate 101 where either the cathode 113 or anode 103 can be in
20 contact with the substrate. The electrode in contact with the substrate 101 is conveniently referred to as the bottom electrode. Conventionally, the bottom electrode is the anode 103, but this invention is not limited to that configuration. The substrate 101 can either be light transmissive or opaque, depending on the intended direction of light emission. The light transmissive property is desirable
25 for viewing the EL emission through the substrate 101. Transparent glass or plastic is commonly employed in such cases. The substrate 101 can be a complex structure comprising multiple layers of materials. This is typically the case for active matrix substrates wherein TFTs are provided below the OLED layers. It is still necessary that the substrate 101, at least in the emissive pixelated areas, be
30 comprised of largely transparent materials such as glass or polymers. For applications where the EL emission is viewed through the top electrode, the

transmissive characteristic of the bottom support is immaterial, and therefore the substrate can be light transmissive, light absorbing or light reflective. Substrates for use in this case include, but are not limited to, glass, plastic, semiconductor materials such as silicon, ceramics, and circuit board materials. Again, the
5 substrate 101 can be a complex structure comprising multiple layers of materials such as found in active matrix TFT designs. It is necessary to provide in these device configurations a light-transparent top electrode.

Anode

When the desired electroluminescent light emission (EL) is viewed
10 through the anode, the anode 103 should be transparent or substantially transparent to the emission of interest. Common transparent anode materials used in this invention are indium-tin oxide (ITO), indium-zinc oxide (IZO) and tin oxide, but other metal oxides can work including, but not limited to, aluminum- or indium-doped zinc oxide, magnesium-indium oxide, and nickel-tungsten oxide.

15 In addition to these oxides, metal nitrides, such as gallium nitride, and metal selenides, such as zinc selenide, and metal sulfides, such as zinc sulfide, can be used as the anode 103. For applications where EL emission is viewed only through the cathode 113, the transmissive characteristics of the anode 103 are immaterial and any conductive material can be used, transparent, opaque or reflective.

20 Example conductors for this application include, but are not limited to, gold, iridium, molybdenum, palladium, and platinum. Typical anode materials, transmissive or otherwise, have a work function of 4.1 eV or greater. Desired anode materials are commonly deposited by any suitable means such as evaporation, sputtering, chemical vapor deposition, or electrochemical means.

25 Anodes can be patterned using well-known photolithographic processes. Optionally, anodes may be polished prior to application of other layers to reduce surface roughness so as to minimize short circuits or enhance reflectivity.

Cathode

When light emission is viewed solely through the anode 103, the
30 cathode 113 used in this invention can be comprised of nearly any conductive material. Desirable materials have good film-forming properties to ensure good contact with the underlying organic layer, promote electron injection at low

voltage, and have good stability. Useful cathode materials often contain a low work function metal (< 4.0 eV) or metal alloy. One useful cathode material is comprised of a Mg:Ag alloy wherein the percentage of silver is in the range of 1 to 20 %, as described in U.S. Patent No. 4,885,221. Another suitable class of cathode materials includes bilayers comprising the cathode and a thin electron-injection layer (EIL) in contact with an organic layer (e.g., an electron transporting layer (ETL)), the cathode being capped with a thicker layer of a conductive metal. Here, the EIL preferably includes a low work function metal or metal salt, and if so, the thicker capping layer does not need to have a low work function. One such cathode is comprised of a thin layer of LiF followed by a thicker layer of Al as described in U.S. Patent No. 5,677,572. An ETL material doped with an alkali metal, for example, Li-doped Alq, is another example of a useful EIL. Other useful cathode material sets include, but are not limited to, those disclosed in U.S. Patent Nos. 5,059,861, 5,059,862, and 6,140,763.

When light emission is viewed through the cathode, the cathode 113 must be transparent or nearly transparent. For such applications, metals must be thin or one must use transparent conductive oxides, or a combination of these materials. Optically transparent cathodes have been described in more detail in US 4,885,211, US 5,247,190, JP 3,234,963, US 5,703,436, US 5,608,287, US 5,837,391, US 5,677,572, US 5,776,622, US 5,776,623, US 5,714,838, US 5,969,474, US 5,739,545, US 5,981,306, US 6,137,223, US 6,140,763, US 6,172,459, EP 1 076 368, US 6,278,236, and US 6,284,3936. Cathode materials are typically deposited by any suitable method such as evaporation, sputtering, or chemical vapor deposition. When needed, patterning can be achieved through many well known methods including, but not limited to, through-mask deposition, integral shadow masking as described in US 5,276,380 and EP 0 732 868, laser ablation, and selective chemical vapor deposition.

Hole-Injecting Layer (HIL)

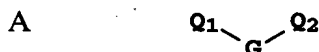
A hole-injecting layer 105 may be provided between anode 103 and hole-transporting layer 107. The hole-injecting layer can serve to improve the film formation property of subsequent organic layers and to facilitate injection of holes

into the hole-transporting layer 107. Suitable materials for use in the hole-injecting layer 105 include, but are not limited to, porphyrinic compounds as described in US 4,720,432, plasma-deposited fluorocarbon polymers as described in US 6,208,075, and some aromatic amines, for example, MTDATA (4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine). Alternative hole-injecting materials reportedly useful in organic EL devices are described in EP 0 891 121 A1 and EP 1 029 909 A1. A hole-injection layer is conveniently used in the present invention, and is desirably a plasma-deposited fluorocarbon polymer. The thickness of a hole-injection layer containing a plasma-deposited fluorocarbon polymer can be in the range of 0.2 nm to 15 nm and suitably in the range of 0.3 to 1.5 nm.

Hole-Transporting Layer (HTL)

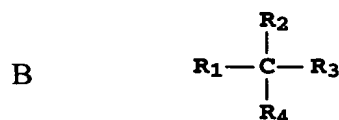
While not always necessary, it is often useful to include a hole-transporting layer in an OLED device. The hole-transporting layer 107 of the organic EL device contains at least one hole-transporting compound such as an aromatic tertiary amine, where the latter is understood to be a compound containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylamin

A more preferred class of aromatic tertiary amines is those which include at least two aromatic tertiary amine moieties as described in US 4,720,432 and US 5,061,569. Such compounds include those represented by structural formula (A).



wherein Q₁ and Q₂ are independently selected aromatic tertiary amine moieties and G is a linking group such as an arylene, cycloalkylene, or alkylene group of a carbon to carbon bond. In one embodiment, at least one of Q₁ or Q₂ contains a polycyclic fused ring structure, e.g., a naphthalene. When G is an aryl group, it is
 5 conveniently a phenylene, biphenylene, or naphthalene moiety.

A useful class of triarylamines satisfying structural formula (A) and containing two triarylamine moieties is represented by structural formula (B):



where

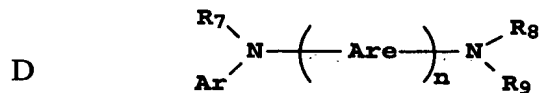
R₁ and R₂ each independently represents a hydrogen atom, an aryl group,
 10 or an alkyl group or R₁ and R₂ together represent the atoms completing a cycloalkyl group; and

R₃ and R₄ each independently represents an aryl group, which is in turn substituted with a diaryl substituted amino group, as indicated by structural formula (C):



15 wherein R₅ and R₆ are independently selected aryl groups. In one embodiment, at least one of R₅ or R₆ contains a polycyclic fused ring structure, e.g., a naphthalene.

Another class of aromatic tertiary amines is the tetraaryldiamines. Desirable tetraaryldiamines include two diarylamino groups, such as indicated by formula (C), linked through an arylene group. Useful tetraaryldiamines include
 20 those represented by formula (D).



wherein

each Are is an independently selected arylene group, such as a phenylene or anthracene moiety,

n is an integer of from 1 to 4, and

Ar, R₇, R₈, and R₉ are independently selected aryl groups.

In a typical embodiment, at least one of Ar, R₇, R₈, and R₉ is a polycyclic fused ring structure, e.g., a naphthalene.

5 The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural formulae (A), (B), (C), (D), can each in turn be substituted. Typical substituents include alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halide such as fluoride, chloride, and bromide. The various alkyl and alkylene moieties typically contain from about 1 to 6 carbon atoms. The
10 cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or seven ring carbon atoms--e.g., cyclopentyl, cyclohexyl, and cycloheptyl ring structures. The aryl and arylene moieties are usually phenyl and phenylene moieties.

 The hole-transporting layer can be formed of a single tertiary amine
15 compound or a mixture of such compounds. Specifically, one may employ a triarylamine, such as a triarylamine satisfying the formula (B), in combination with a tetraaryldiamine, such as indicated by formula (D). Illustrative of useful aromatic tertiary amines are the following:

 1,1-Bis(4-di-*p*-tolylaminophenyl)cyclohexane (TAPC)
20 1,1-Bis(4-di-*p*-tolylaminophenyl)-4-methylcyclohexane
 1,1-Bis(4-di-*p*-tolylaminophenyl)-4-phenylcyclohexane
 1,1-Bis(4-di-*p*-tolylaminophenyl)-3-phenylpropane (TAPPP)
 N,N,N',N'-tetraphenyl-4,4'''-diamino-1,1':4',1'':4'',1'''-quaterphenyl
 Bis(4-dimethylamino-2-methylphenyl)phenylmethane
25 1,4-bis[2-[4-[*N,N*-di(*p*-tolyl)amino]phenyl]vinyl]benzene (BDTAPVB)
 N,N,N',N'-Tetra-*p*-tolyl-4,4'-diaminobiphenyl (TTB)
 N,N,N',N'-Tetraphenyl-4,4'-diaminobiphenyl
 N,N,N',N'-tetra-1-naphthyl-4,4'-diaminobiphenyl
 N,N,N',N'-tetra-2-naphthyl-4,4'-diaminobiphenyl
30 *N*-Phenylcarbazole
 4,4'-Bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB)

4,4'-Bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]biphenyl (TNB)
 4,4'-Bis[*N*-(1-naphthyl)-*N*-phenylamino]*p*-terphenyl
 4,4'-Bis[*N*-(2-naphthyl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(3-acenaphthenyl)-*N*-phenylamino]biphenyl
 5 1,5-Bis[*N*-(1-naphthyl)-*N*-phenylamino]naphthalene
 4,4'-Bis[*N*-(9-anthryl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(1-anthryl)-*N*-phenylamino]-*p*-terphenyl
 4,4'-Bis[*N*-(2-phenanthryl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(8-fluoranthenyl)-*N*-phenylamino]biphenyl
 10 4,4'-Bis[*N*-(2-pyrenyl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(2-naphthacenyl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(2-perylenyl)-*N*-phenylamino]biphenyl
 4,4'-Bis[*N*-(1-coronenyl)-*N*-phenylamino]biphenyl
 2,6-Bis(di-*p*-tolylamino)naphthalene
 15 2,6-Bis[di-(1-naphthyl)amino]naphthalene
 2,6-Bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]naphthalene
N,N,N',N'-Tetra(2-naphthyl)-4,4''-diamino-*p*-terphenyl
 4,4'-Bis{*N*-phenyl-*N*-[4-(1-naphthyl)-phenyl]amino}biphenyl
 2,6-Bis[*N,N*-di(2-naphthyl)amino]fluorene
 20 4,4',4''-tris[(3-methylphenyl)phenylamino]triphenylamine (MTDATA)
 4,4'-Bis[*N*-(3-methylphenyl)-*N*-phenylamino]biphenyl (TPD)

Another class of useful hole-transporting materials includes polycyclic aromatic compounds as described in EP 1 009 041. Tertiary aromatic amines with more than two amine groups may be used including oligomeric
 25 materials. In addition, polymeric hole-transporting materials can be used such as poly(*N*-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, and copolymers such as poly(3,4-ethylenedioxythiophene) / poly(4-styrenesulfonate) also called PEDOT/PSS. It is also possible for the hole-transporting layer to comprise two or more sublayers of differing compositions, the composition of
 30 each sublayer being as described above. The thickness of the hole-transporting layer can be between 10 and about 500 nm and suitably between 50 and 300 nm.

Light-Emitting Layer (LEL)

In addition to the light-emitting materials of this invention, additional light emitting materials may be used in the EL device, including other fluorescent materials. Other fluorescent materials may be used in the same layer as the boron complex material, in adjacent layers, in adjacent pixels, or any combination.

As more fully described in U.S. Patent Nos. 4,769,292 and 5,935,721, the light-emitting layer (LEL) of the organic EL element includes a luminescent material where electroluminescence is produced as a result of electron-hole pair recombination. The light-emitting layer can be comprised of a single material, but more commonly consists of a host material doped with a guest emitting material or materials where light emission comes primarily from the emitting materials and can be of any color. The host materials in the light-emitting layer can be an electron-transporting material, as defined below, a hole-transporting material, as defined above, or another material or combination of materials that support hole-electron recombination. Fluorescent emitting materials are typically incorporated at 0.01 to 10 % by weight of the host material.

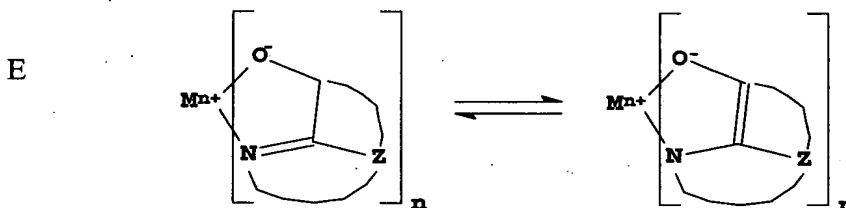
The host and emitting materials can be small non-polymeric molecules or polymeric materials such as polyfluorenes and polyvinylarylenes (e.g., poly(*p*-phenylenevinylene), PPV). In the case of polymers, small-molecule emitting materials can be molecularly dispersed into a polymeric host, or the emitting materials can be added by copolymerizing a minor constituent into a host polymer. Host materials may be mixed together in order to improve film formation, electrical properties, light emission efficiency, operating lifetime, or manufacturability. The host may comprise a material that has good hole-transporting properties and a material that has good electron-transporting properties.

An important relationship for choosing a fluorescent material as a guest emitting material is a comparison of the excited singlet-state energies of the host and the fluorescent material. It is highly desirable that the excited singlet-state energy of the fluorescent material be lower than that of the host material.

The excited singlet-state energy is defined as the difference in energy between the emitting singlet state and the ground state. For non-emissive hosts, the lowest excited state of the same electronic spin as the ground state is considered the emitting state.

Host and emitting materials known to be of use include, but are not limited to, those disclosed in US 4,768,292, US 5,141,671, US 5,150,006, US 5,151,629, US 5,405,709, US 5,484,922, US 5,593,788, US 5,645,948, US 5,683,823, US 5,755,999, US 5,928,802, US 5,935,720, US 5,935,721, and US 6,020,078.

Metal complexes of 8-hydroxyquinoline and similar derivatives, also known as metal-chelated oxinoid compounds (Formula E), constitute one class of useful host compounds capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 500 nm, e.g., green, yellow, orange, and red.



wherein

M represents a metal;

n is an integer of from 1 to 4; and

Z independently in each occurrence represents the atoms completing a nucleus having at least two fused aromatic rings.

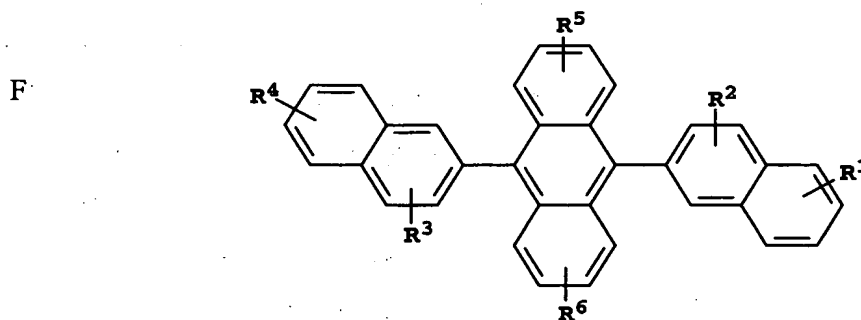
From the foregoing it is apparent that the metal can be monovalent, divalent, trivalent, or tetravalent metal. The metal can, for example, be an alkali metal, such as lithium, sodium, or potassium; an alkaline earth metal, such as magnesium or calcium; a trivalent metal, such aluminum or gallium, or another metal such as zinc or zirconium. Generally any monovalent, divalent, trivalent, or tetravalent metal known to be a useful chelating metal can be employed.

Z completes a heterocyclic nucleus containing at least two fused aromatic rings, at least one of which is an azole or azine ring. Additional rings, including both aliphatic and aromatic rings, can be fused with the two required rings, if required. To avoid adding molecular bulk without improving on function
5 the number of ring atoms is usually maintained at 18 or less.

Illustrative of useful chelated oxinoid compounds are the following:

- CO-1: Aluminum trisoxine [alias, tris(8-quinolinolato)aluminum(III)]
CO-2: Magnesium bisoxine [alias, bis(8-quinolinolato)magnesium(II)]
10 CO-3: Bis[benzo {f} -8-quinolinolato]zinc (II)
CO-4: Bis(2-methyl-8-quinolinolato)aluminum(III)- μ -oxo-bis(2-methyl-8-quinolinolato) aluminum(III)
CO-5: Indium trisoxine [alias, tris(8-quinolinolato)indium]
CO-6: Aluminum tris(5-methyloxine) [alias, tris(5-methyl-8-quinolinolato)
15 aluminum(III)]
CO-7: Lithium oxine [alias, (8-quinolinolato)lithium(I)]
CO-8: Gallium oxine [alias, tris(8-quinolinolato)gallium(III)]
CO-9: Zirconium oxine [alias, tetra(8-quinolinolato)zirconium(IV)]

As already mentioned, derivatives of 9,10-di-(2-
20 naphthyl)anthracene (Formula F) constitute one class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g., blue, green, yellow, orange or red.



wherein: R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 represent one or more substituents on each ring where each substituent is individually selected from the following groups:

Group 1: hydrogen, or alkyl of from 1 to 24 carbon atoms;

Group 2: aryl or substituted aryl of from 5 to 20 carbon atoms;

5 Group 3: carbon atoms from 4 to 24 necessary to complete a fused aromatic ring of anthracenyl; pyrenyl, or perylenyl;

Group 4: heteroaryl or substituted heteroaryl of from 5 to 24 carbon atoms as necessary to complete a fused heteroaromatic ring of furyl, thienyl, pyridyl, quinolinyl or other heterocyclic systems;

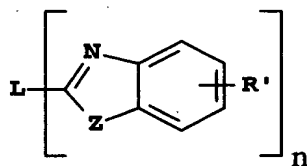
10 Group 5: alkoxyamino, alkylamino, or arylamino of from 1 to 24 carbon atoms; and

Group 6: fluorine, chlorine, bromine or cyano.

Illustrative examples include 9,10-di-(2-naphthyl)anthracene and 2-*t*-butyl-9,10-di-(2-naphthyl)anthracene. Other anthracene derivatives can be useful
15 as a host in the LEL, including derivatives of 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene.

Benzazole derivatives (Formula G) constitute another class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g.,
20 blue, green, yellow, orange or red.

G



wherein:

n is an integer of 3 to 8;

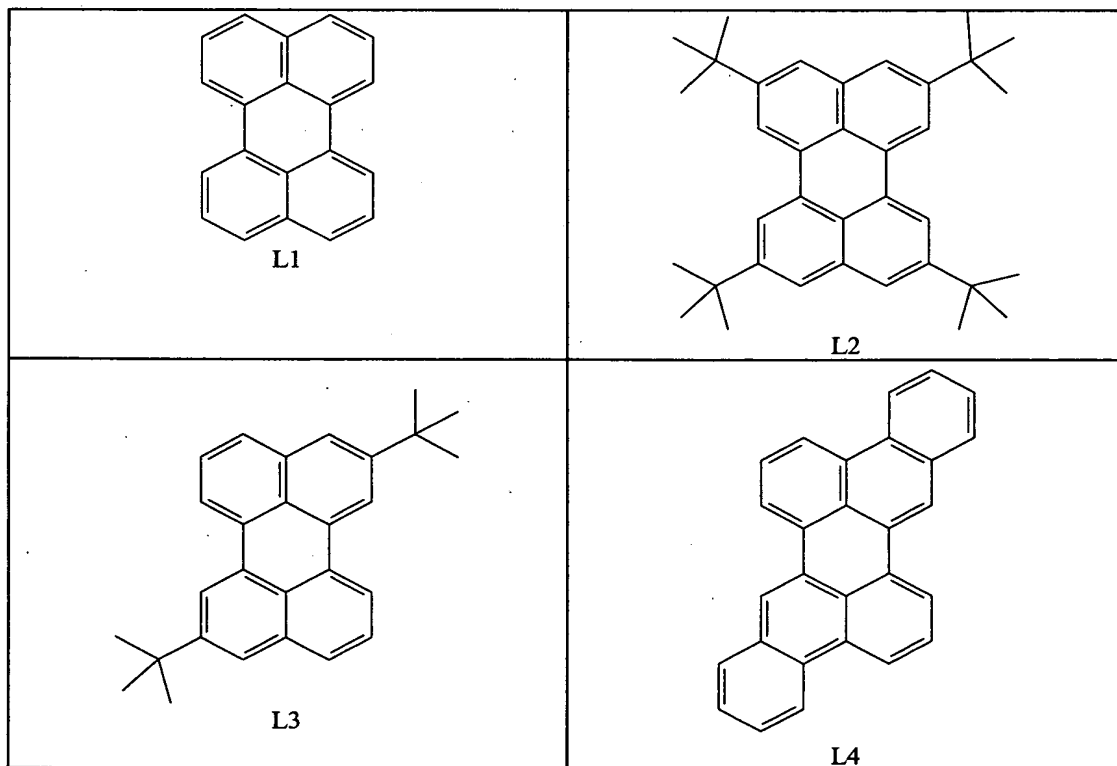
Z is O, NR or S; and

R and R' are individually hydrogen; alkyl of from 1 to 24 carbon atoms, for example, propyl, *t*-butyl, heptyl, and the like; aryl or hetero-atom substituted
25 aryl of from 5 to 20 carbon atoms for example phenyl and naphthyl, furyl, thienyl, pyridyl, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring; and

L is a linkage unit consisting of alkyl, aryl, substituted alkyl, or substituted aryl, which connects the multiple benzazoles together. L may be either conjugated with the multiple benzazoles or not in conjugation with them. An example of a useful benzazole is 2,2',2''-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole].

5 Styrylarylene derivatives as described in U.S. Patent 5,121,029 and JP 08333569 are also useful hosts for blue emission. For example, 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene and 4,4'-bis(2,2-diphenylethenyl)-1,1'-biphenyl (DPVBi) are useful hosts for blue emission.

Useful fluorescent emitting materials include, but are not limited to, derivatives of anthracene, tetracene, xanthene, perylene, rubrene, coumarin, rhodamine, and quinacridone, dicyanomethylenepyran compounds, thiopyran compounds, polymethine compounds, pyrylium and thiapyrylium compounds, fluorene derivatives, perflanthene derivatives, indenoperylene derivatives, bis(azinyl)amine boron compounds, bis(azinyl)methane compounds, and
10 carbostyryl compounds. Illustrative examples of useful materials include, but are not limited to, the following:



L5

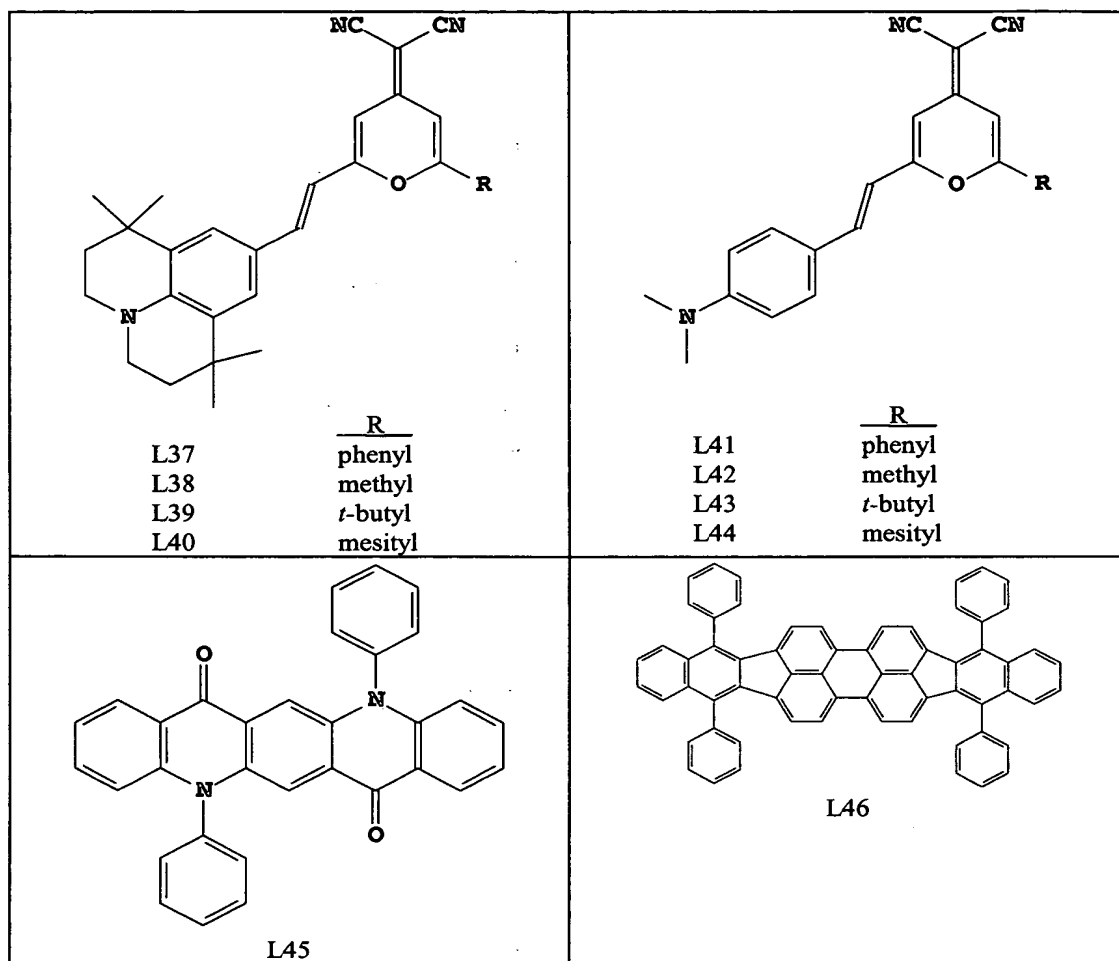
L6

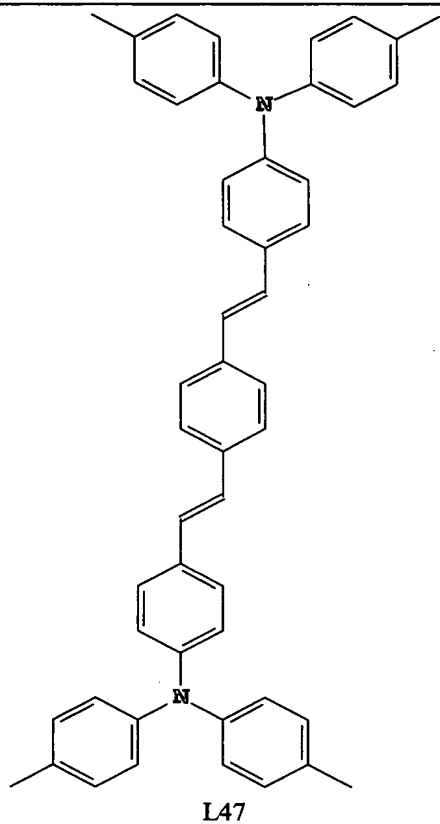
L7

L8

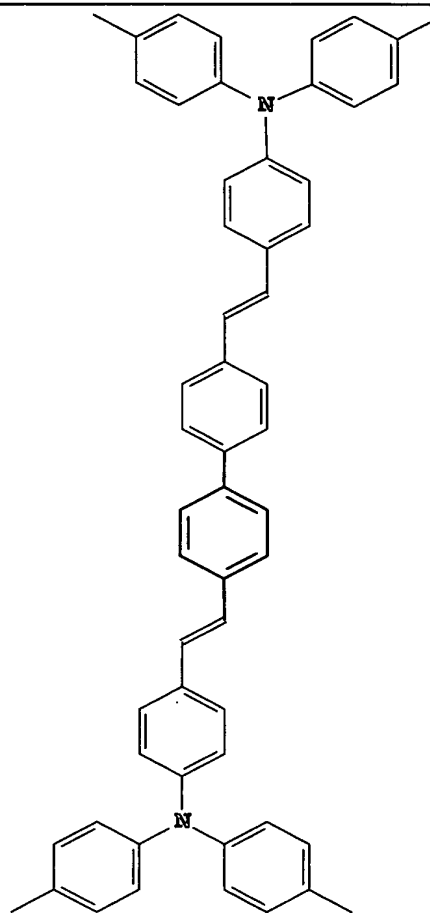
	<u>X</u>	<u>R1</u>	<u>R2</u>
L9	O	H	H
L10	O	H	Methyl
L11	O	Methyl	H
L12	O	Methyl	Methyl
L13	O	H	<i>t</i> -butyl
L14	O	<i>t</i> -butyl	H
L15	O	<i>t</i> -butyl	<i>t</i> -butyl
L16	S	H	H
L17	S	H	Methyl
L18	S	Methyl	H
L19	S	Methyl	Methyl
L20	S	H	<i>t</i> -butyl
L21	S	<i>t</i> -butyl	H
L22	S	<i>t</i> -butyl	<i>t</i> -butyl

	<u>X</u>	<u>R1</u>	<u>R2</u>
L23	O	H	H
L24	O	H	Methyl
L25	O	Methyl	H
L26	O	Methyl	Methyl
L27	O	H	<i>t</i> -butyl
L28	O	<i>t</i> -butyl	H
L29	O	<i>t</i> -butyl	<i>t</i> -butyl
L30	S	H	H
L31	S	H	Methyl
L32	S	Methyl	H
L33	S	Methyl	Methyl
L34	S	H	<i>t</i> -butyl
L35	S	<i>t</i> -butyl	H
L36	S	<i>t</i> -butyl	<i>t</i> -butyl

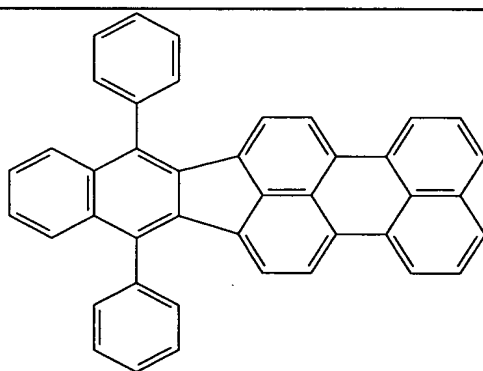




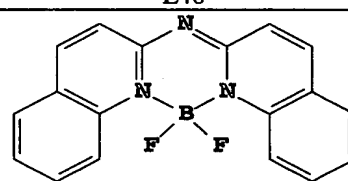
L47



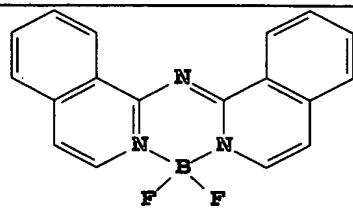
L48



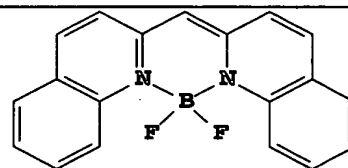
L49



L50



L51



L52

In addition to the light-emitting materials of this invention, light-emitting phosphorescent materials may be used in the EL device. For convenience, the phosphorescent complex guest material may be referred to herein as a phosphorescent material. The phosphorescent material typically includes one or more ligands, for example monoanionic ligands that can be coordinated to a metal through an sp^2 carbon and a heteroatom. Conveniently, the ligand can be phenylpyridine (ppy) or derivatives or analogs thereof. Examples of some useful phosphorescent organometallic materials include tris(2-phenylpyridinato- N,C^2')iridium(III), bis(2-phenylpyridinato- N,C^2')iridium(III)(acetylacetonate), and bis(2-phenylpyridinato- N,C^2')platinum(II). Usefully, many phosphorescent organometallic materials emit in the green region of the spectrum, that is, with a maximum emission in the range of 510 to 570 nm.

Phosphorescent materials may be used singly or in combinations with other phosphorescent materials, either in the same or different layers.

Phosphorescent materials and suitable hosts are described in WO 00/57676, WO 00/70655, WO 01/41512 A1, WO 02/15645 A1, US 2003/0017361 A1, WO 01/93642 A1, WO 01/39234 A2, US 6,458,475 B1, WO 02/071813 A1, US 6,573,651 B2, US 2002/0197511 A1, WO 02/074015 A2, US 6,451,455 B1, US 2003/0072964 A1, US 2003/0068528 A1, US 6,413,656 B1, US 6,515,298 B2, US 6,451,415 B1, US 6,097,147, US 2003/0124381 A1, US 2003/0059646 A1, US 2003/0054198 A1, EP 1 239 526 A2, EP 1 238 981 A2, EP 1 244 155 A2, US 2002/0100906 A1, US 2003/0068526 A1, US 2003/0068535 A1, JP 2003073387A, JP 2003 073388A, US 2003/0141809 A1, US 2003/0040627 A1, JP 2003059667A, JP 2003073665A, and US 2002/0121638 A1.

The emission wavelengths of cyclometallated Ir(III) complexes of the type IrL_3 and IrL_2L' , such as the green-emitting *fac*-tris(2-phenylpyridinato- N,C^2')iridium(III) and bis(2-phenylpyridinato- N,C^2')iridium(III)(acetylacetonate) may be shifted by substitution of electron donating or withdrawing groups at appropriate positions on the cyclometallating ligand L, or by choice of different heterocycles for the cyclometallating ligand L. The emission wavelengths may also be shifted by choice of the ancillary ligand L'. Examples of red emitters are

the bis(2-(2'-benzothienyl)pyridinato-*N,C*^{3'})iridium(III)(acetylacetonate) and tris(2-phenylisoquinolino-*N,C*)iridium(III). A blue-emitting example is bis(2-(4,6-difluorophenyl)-pyridinato-*N,C*^{2'})iridium(III)(picolinate).

Red electrophosphorescence has been reported, using bis(2-(2'-benzo[4,5-a]thienyl)pyridinato-*N,C*^{3'}) iridium (acetylacetonate) [Btp₂Ir(acac)] as the phosphorescent material (C. Adachi, S. Lamansky, M. A. Baldo, R. C. Kwong, M. E. Thompson, and S. R. Forrest, *App. Phys. Lett.*, **78**, 1622-1624 (2001)).

Other important phosphorescent materials include cyclometallated Pt(II) complexes such as cis-bis(2-phenylpyridinato-*N,C*^{2'})platinum(II), cis-bis(2-(2'-thienyl)pyridinato-*N,C*^{3'}) platinum(II), cis-bis(2-(2'-thienyl)quinolino-*N,C*^{5'}) platinum(II), or (2-(4,6-difluorophenyl)pyridinato-*N,C*^{2'}) platinum (II) (acetylacetonate). Pt (II) porphyrin complexes such as 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphine platinum(II) are also useful phosphorescent materials.

Still other examples of useful phosphorescent materials include coordination complexes of the trivalent lanthanides such as Tb³⁺ and Eu³⁺ (J. Kido et al., *Appl. Phys. Lett.*, **65**, 2124 (1994)).

Suitable host materials for phosphorescent materials should be selected so that transfer of a triplet exciton can occur efficiently from the host material to the phosphorescent material but cannot occur efficiently from the phosphorescent material to the host material. Therefore, it is highly desirable that the triplet energy of the phosphorescent material be lower than the triplet energy of the host. Generally speaking, a large triplet energy implies a large optical bandgap. However, the band gap of the host should not be chosen so large as to cause an unacceptable barrier to injection of charge carriers into the light-emitting layer and an unacceptable increase in the drive voltage of the OLED. Suitable host materials are described in WO 00/70655 A2; 01/39234 A2; 01/ 93642 A1; 02/074015 A2; 02/15645 A1, and US 20020117662. Suitable hosts include certain aryl amines, triazoles, indoles and carbazole compounds. Examples of desirable hosts are 4,4'-*N,N'*-dicarbazole-biphenyl, otherwise known as 4,4'-bis(carbazol-9-yl)biphenyl or CBP; 4,4'-*N,N'*-dicarbazole-2,2'-dimethyl-biphenyl, otherwise known as 2,2'-

dimethyl-4,4'-bis(carbazol-9-yl)biphenyl or CDBP; 1,3-bis(*N,N'*-dicarbazole)benzene, otherwise known as 1,3-bis(carbazol-9-yl)benzene, and poly(*N*-vinylcarbazole), including their derivatives.

Desirable host materials are capable of forming a continuous film.

5 Hole-Blocking Layer (HBL)

In addition to suitable hosts, an OLED device employing a phosphorescent material often requires at least one hole-blocking layer placed between the electron-transporting layer 111 and the light-emitting layer 109 to help confine the excitons and recombination events to the light-emitting layer comprising the host and phosphorescent material. In this case, there should be an energy barrier for hole migration from the host into the hole-blocking layer, while electrons should pass readily from the hole-blocking layer into the light-emitting layer comprising a host and a phosphorescent material. The first requirement entails that the ionization potential of the hole-blocking layer be larger than that of the light-emitting layer 109, desirably by 0.2 eV or more. The second requirement entails that the electron affinity of the hole-blocking layer not greatly exceed that of the light-emitting layer 109, and desirably be either less than that of light-emitting layer or not exceed that of the light-emitting layer by more than about 0.2 eV.

20 When used with an electron-transporting layer whose characteristic luminescence is green, such as an Alq-containing electron-transporting layer as described below, the requirements concerning the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the material of the hole-blocking layer frequently result in a characteristic luminescence of the hole-blocking layer at shorter wavelengths than that of the electron-transporting layer, such as blue, violet, or ultraviolet luminescence. Thus, it is desirable that the characteristic luminescence of the material of a hole-blocking layer be blue, violet, or ultraviolet. It is further desirable, but not absolutely required, that the triplet energy of the hole-blocking material be greater than that of the phosphorescent material. Suitable hole-blocking materials are described in WO 00/70655A2 and WO 01/93642 A1. Two examples of useful

hole-blocking materials are bathocuproine (BCP) and bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminum(III) (BAIq). The characteristic luminescence of BCP is in the ultraviolet, and that of BAIq is blue. Metal complexes other than BAIq are also known to block holes and excitons as described in US 20030068528. In addition, US 20030175553 A1 describes the use of *fac*-tris(1-phenylpyrazolato-*N,C*^{2'})iridium(III) (Irppz) for this purpose.

When a hole-blocking layer is used, its thickness can be between 2 and 100 nm and suitably between 5 and 10 nm.

Electron-Transporting Layer (ETL)

Desirable thin film-forming materials for use in forming the electron-transporting layer 111 of the organic EL devices of this invention are metal-chelated oxinoid compounds, including chelates of oxine itself (also commonly referred to as 8-quinolinol or 8-hydroxyquinoline). Such compounds help to inject and transport electrons, exhibit high levels of performance, and are readily fabricated in the form of thin films. Exemplary of contemplated oxinoid compounds are those satisfying structural formula (E), previously described.

Other electron-transporting materials suitable for use in the electron-transporting layer 111 include various butadiene derivatives as disclosed in US 4,356,429 and various heterocyclic optical brighteners as described in US 4,539,507. Benzazoles satisfying structural formula (G) are also useful electron transporting materials. Triazines are also known to be useful as electron transporting materials.

If both a hole-blocking layer and an electron-transporting layer 111 are used, electrons should pass readily from the electron-transporting layer 111 into the hole-blocking layer. Therefore, the electron affinity of the electron-transporting layer 111 should not greatly exceed that of the hole-blocking layer. Desirably, the electron affinity of the electron-transporting layer should be less than that of the hole-blocking layer or not exceed it by more than about 0.2 eV.

If an electron-transporting layer is used, its thickness may be between 2 and 100 nm and suitably between 5 and 20 nm.

Other Useful Organic Layers and Device Architecture

In some instances, layers 109 through 111 can optionally be collapsed into a single layer that serves the function of supporting both light emission and electron transportation. The hole-blocking layer, when present, and layer 111 may also be collapsed into a single layer that functions to block holes or excitons, and supports electron transport. It also known in the art that emitting materials may be included in the hole-transporting layer 107. In that case, the hole-transporting material may serve as a host. Multiple materials may be added to one or more layers in order to create a white-emitting OLED, for example, by combining blue- and yellow-emitting materials, cyan- and red-emitting materials, or red-, green-, and blue-emitting materials. White-emitting devices are described, for example, in EP 1 187 235, US 20020025419, EP 1 182 244, US 5,683,823, US 5,503,910, US 5,405,709, and US 5,283,182 and can be equipped with a suitable filter arrangement to produce a color emission.

This invention may be used in so-called stacked device architecture, for example, as taught in US 5,703,436 and US 6,337,492.

Deposition of Organic Layers

The organic materials mentioned above are suitably deposited by any means suitable for the form of the organic materials. In the case of small molecules, they are conveniently deposited through sublimation or evaporation, but can be deposited by other means such as coating from a solvent together with an optional binder to improve film formation. If the material is a polymer, solvent deposition is usually preferred. The material to be deposited by sublimation or evaporation can be vaporized from a sublimator "boat" often comprised of a tantalum material, e.g., as described in US 6,237,529, or can be first coated onto a donor sheet and then sublimed in closer proximity to the substrate. Layers with a mixture of materials can utilize separate sublimator boats or the materials can be pre-mixed and coated from a single boat or donor sheet. Patterned deposition can be achieved using shadow masks, integral shadow masks (US 5,294,870), spatially-defined thermal dye transfer from a donor sheet (US 5,688,551, US 5,851,709 and US 6,066,357) or an inkjet method (US 6,066,357).

Encapsulation

Most OLED devices are sensitive to moisture or oxygen, or both, so they are commonly sealed in an inert atmosphere such as nitrogen or argon, along with a desiccant such as alumina, bauxite, calcium sulfate, clays, silica gel, zeolites, alkaline metal oxides, alkaline earth metal oxides, sulfates, or metal halides and perchlorates. Methods for encapsulation and desiccation include, but are not limited to, those described in U.S. Patent No. 6,226,890. In addition, barrier layers such as SiO_x, Teflon, and alternating inorganic/polymeric layers are known in the art for encapsulation. Any of these methods of sealing or encapsulation and desiccation can be used with the EL devices constructed according to the present invention.

Optical Optimization

OLED devices of this invention can employ various well-known optical effects in order to enhance their emissive properties if desired. This includes optimizing layer thicknesses to yield maximum light transmission, providing dielectric mirror structures, replacing reflective electrodes with light-absorbing electrodes, providing anti-glare or anti-reflection coatings over the display, providing a polarizing medium over the display, or providing colored, neutral density, or color-conversion filters over the display. Filters, polarizers, and anti-glare or anti-reflection coatings may be specifically provided over the EL device or as part of the EL device.

Embodiments of the invention may provide advantageous features such as higher luminous yield, lower drive voltage, higher power efficiency, improved stability, reduced sublimation temperatures, and simplified manufacturing, as well as desirable hues including those useful in the emission of white light (directly or through filters to provide multicolor displays). Embodiments of the invention can also provide devices incorporating the OLED device such as electronic displays and area lighting devices.

The invention and its advantages can be better appreciated by the following examples.

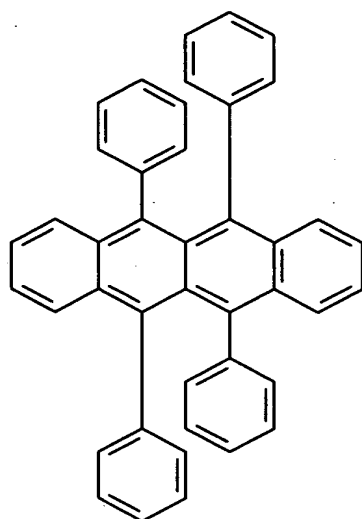
Synthetic Example: Preparation of Inv-1.

1-Bromo-3-fluorobenzene (6.3g, 36.5 mmol) was dissolved in 40 mL THF and cooled to -78°C under a positive pressure of nitrogen. *n*-BuLi (1.6 M in hexanes; 35.1 mmol) was added dropwise, and the solution was stirred for 30 min before being transferred via cannula to a solution of 6,11-diphenyl-5,12-naphthacenequinone (3g, 7.3 mmol) in THF at -78°C . The reaction was warmed to 25°C , and quenched with methanol. The product was partitioned between methylene chloride and water. The organic layers were dried over MgSO_4 , filtered, and then concentrated to an oil. The oil was triturated with ether and hexane to produce 3.7g of diol at 97% purity by HPLC analysis. The diol was suspended in 150 mL ether. A solution of hydrogen iodide in water (10.5 mmol) was added, and the reaction was refluxed for 5 min. After cooling, excess sodium metabisulfite was added and the product was extracted into methylene chloride. The organic layers were dried and concentrated to produce a red solid. After chromatography, the 1.7 g of the tetracene, Inv 1-1, was isolated. The structure was consistent with NMR and mass spectrometry data and was confirmed by X-ray analysis.

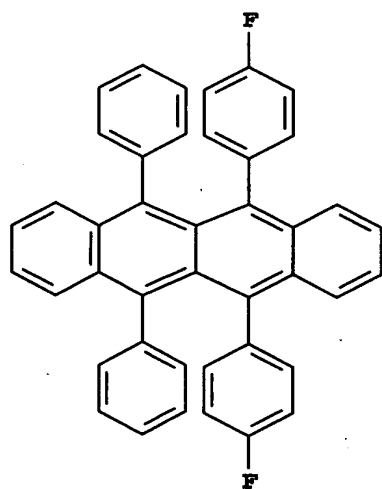
Sublimation Temperatures Example:

The sublimation temperatures at 5×10^{-6} Torr needed to deposit the inventive and comparative dopants at 1% and 2%-wt. of the host are recorded in Table 1. This sublimation temperature is the temperature required to sublime a specific amount of material, recorded as thickness, onto the device at a specific rate and is given in Angstroms/sec., (A/s). For dopants at 1%-wt of host, this rate is 0.04A/s and at 2%-wt it is 0.08A/s.

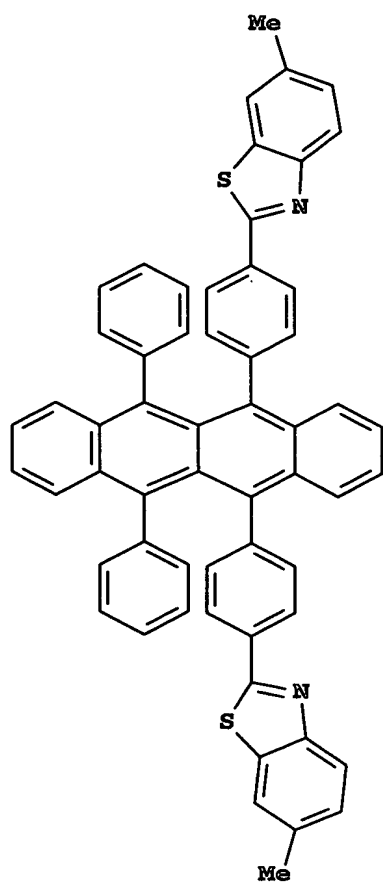
The comparative compounds used in the invention are listed below. Com-1 is the parent rubrene compound. Com-2 is the para-fluoro substituted isomer of Inv-1. Com-3 and Com-4 are other yellow dopants known in the literature.



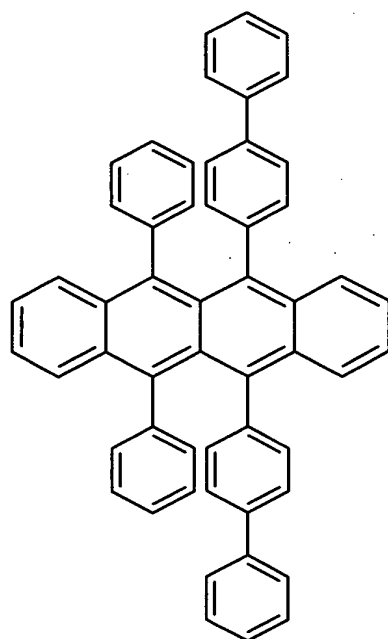
Com-1



Com-2



Com-3



Com-4

TABLE 1: SUBLIMATION TEMPERATURES

Sample	Type	Dopant	Sublimation Temp (°C) Dopant Level	
			1%	2%
1-1	Inventive	Inv-1	186	197
1-2	Comparative	Com-1	211	218
1-3	Comparative	Com-2	201	203
1-4	Comparative	Com-3	-	327
1-5	Inventive	Inv-10	238	249
1-6	Comparative	Com-4	255	262
1-7	Inventive	Inv-18	245	255

It can be seen from Table 1 that the materials of the invention have lower sublimation temperatures relative to comparison materials having similar structures. For example Inv-1 sublimates at a lower temperature than Com-1 or Com-2. Inv-10 sublimates at a lower temperature than Com-3 or Com-4, and Inv-18 sublimates at a temperature significantly lower than that of the close analog, Com-3.

It can be seen from Table 1 that the tested materials of the invention have lower sublimation temperatures relative to comparison materials having similar structures. For example Inv-1 sublimates at a lower temperature than Com-1 or Com-2. Inv-10 sublimates at a lower temperature than Com-3 or Com-4, and Inv-18 sublimates at a temperature significantly lower than the close analog, Com-3.

Device Example 1: EL Device Fabrication of Samples 1-4.

An EL device (Sample 1) satisfying the requirements of the invention was constructed in the following manner:

1. A glass substrate coated with an 85 nm layer of indium-tin oxide (ITO) as the anode was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water,

degreased in toluene vapor and exposed to oxygen plasma for about 1 min.

2. Over the ITO was deposited a 1 nm fluorocarbon (CFx) hole-injecting layer (HIL) by plasma-assisted deposition of CHF₃.
3. A hole-transporting layer (HTL) of *N,N'*-di-1-naphthyl-*N,N'*-diphenyl-4,4'-diaminobiphenyl (NPB) having a thickness of 150 Å was then evaporated from a tantalum boat.
4. A 37.5 nm light-emitting layer (LEL) of tris(8-quinolinolato)aluminum (III) (AlQ₃) and Inv-1 (1.0%) were then deposited onto the hole-transporting layer. These materials were also evaporated from tantalum boats.
5. A 37.5 nm electron-transporting layer (ETL) of tris(8-quinolinolato)aluminum (III) (AlQ₃) was then deposited onto the light-emitting layer. This material was also evaporated from a tantalum boat.
6. On top of the AlQ₃ layer was deposited a 220 nm cathode formed of a 10:1 volume ratio of Mg and Ag.

The above sequence completed the deposition of the EL device.

The device was then hermetically packaged in a dry glove box for protection against ambient environment.

EL devices, Samples 2-4, incorporating Inv-1 were fabricated in an identical manner as Sample 1, except Inv-1 was used at the levels indicated in the Table 2. The cells thus formed were tested for luminance and color at an operating current of 20 mA/cm² and the results are reported in Table 2 in the form of luminance yield (cd/A), λ_{max} of emission, and CIE (Commission Internationale de L'Eclairage) coordinates of the emission.

TABLE 2. EVALUATION RESULTS FOR EL DEVICES 1-4 .

Sample	Material	Level (%)	Yield (cd/A)	λ_{max} (nm)	CIE _x	CIE _y	Type
1	Inv-1	1.00	7.04	560	0.479	0.507	Invention
2	Inv-1	2.00	6.44	564	0.502	0.490	Invention
3	Inv-1	3.00	5.82	568	0.509	0.484	Invention
4	Inv-1	5.00	4.91	568	0.517	0.476	Invention

As can be seen from Table 2, tested devices incorporating the invention light-emitting material, Inv-1, demonstrate good efficiency and color.

Device Example 2: EL Device Fabrication of Samples 5-12.

EL devices, Samples 5-12, were fabricated in an identical as Samples 1-4, except Inv-10 was used in place of Inv-1. The cells thus formed were tested for luminance and color at an operating current of 20 mA/cm² and the results are reported in Table 3 in the form of luminance yield (cd/A), λ_{max} of emission, and CIE coordinates of the emission.

TABLE 3. EVALUATION RESULTS FOR EL DEVICES 5-8.

Sample	Material	Level (%)	Yield (cd/A)	λ_{max} (nm)	CIE _x	CIE _y	Type
5	Inv-10	1.00	8.87	564	0.484	0.505	Invention
6	Inv-10	2.00	8.60	560	0.463	0.520	Invention
7	Inv-10	3.00	8.14	568	0.494	0.497	Invention
8	Inv-10	5.00	6.88	572	0.508	0.484	Invention
9	Com-4	1.00	8.32	568	0.507	0.484	Comparative
10	Com-4	2.00	8.19	572	0.522	0.473	Comparative
11	Com-4	3.00	7.18	576	0.532	0.463	Comparative
12	Com-4	5.00	6.29	576	0.541	0.454	Comparative

As can be seen from Table 3, tested devices incorporating the invention light-emitting material, Inv-10, demonstrate good efficiency and color, and that the efficiency of Inv-10 is superior to that of Com-4.

The entire contents of the patents and other publications referred to in this specification are incorporated herein by reference. The invention has been

described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

PARTS LIST

101	Substrate
103	Anode
105	Hole-Injecting layer (HIL)
107	Hole-Transporting layer (HTL)
109	Light-Emitting layer (LEL)
111	Electron-Transporting layer (ETL)
113	Cathode